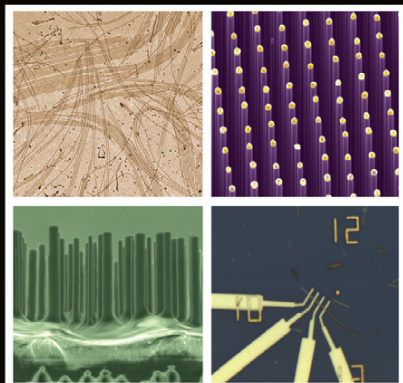




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Materials, Synthesis,
Characterization and Applications

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Woodhead Publishing Series in Electronic
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Jordi Arbiol and Qihua Xiong



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British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

Library of Congress Control Number: 2014957595

ISBN 978-1-78242-253-2 (print)

ISBN 978-1-78242-263-1 (online)

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Part One

Semiconductor materials for nanowires

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II–VI semiconductor nanowires: ZnO

1

J. Miao, B. Liu

School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore

1.1 Introduction

II–VI semiconductors such as ZnS, CdS, and CdTe are a special class of materials with properties in between those of insulators and conductors, comprising elements of Groups II and VI of the Periodic Table, among which zinc oxide (ZnO) is an important II–VI semiconductor material that has been used in a wide range of applications. The first application of ZnO dates to a few thousand years ago, in the Bronze Age, when people started using it to heal wounds. Later, the Romans learned to use ZnO in brass production, although the exact ingredients were unknown. Nowadays, ZnO is an essential component that appears in various products, such as plastics, ceramics, rubbers, lubricants, batteries, paints, protective coatings, fire retardants, and pharmaceutical products (Figure 1.1).

In modern materials science, ZnO is an important II–VI semiconductor with several unique features, including the wide bandgap (3.37 eV), good transparency, excellent electron mobility, and low thermal expansion, which make ZnO a versatile

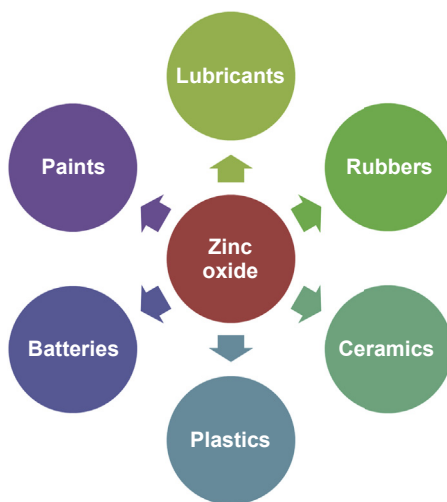


Figure 1.1 The application areas of ZnO.

material in numerous novel applications, such as light-emitting diodes, ultraviolet (UV) lasers, solar cells, solar water splitting cells, biosensors, and piezoelectronics.

Over the past two decades, materials scientists have developed various synthetic means for preparing ZnO nanostructures. ZnO nanoparticles, nanowires, nanobelts, nanoflowers, etc. can now be readily synthesized using various synthetic methods and strategies, such as hydrothermal, electrochemical deposition, physical and chemical vapor deposition, sputtering, atomic layer deposition, and spray pyrolysis. [Figure 1.2](#) shows a classic collection of nanostructured ZnO with different morphologies obtained by thermal evaporation of ZnO powders ([Wang, 2004a](#)).

Among all nanostructures of ZnO, one-dimensional (1D) ZnO nanostructures, such as nanowires, nanotubes, and nanobelts, have been most intensively studied, owing to their unique properties and potential applications. 1D nanostructures can serve as model systems to investigate the dimensional dependence of electrical and thermal transport on the quantum confinement regime as well as play important roles as interconnects or functional units in fabricating nanoscale devices ([Xia et al., 2003](#)).

In this chapter, recent advances in shape-controlled synthesis of 1D ZnO nanostructures and their applications are highlighted, with the aim of introducing new insights into the design and application of 1D ZnO nanostructures.

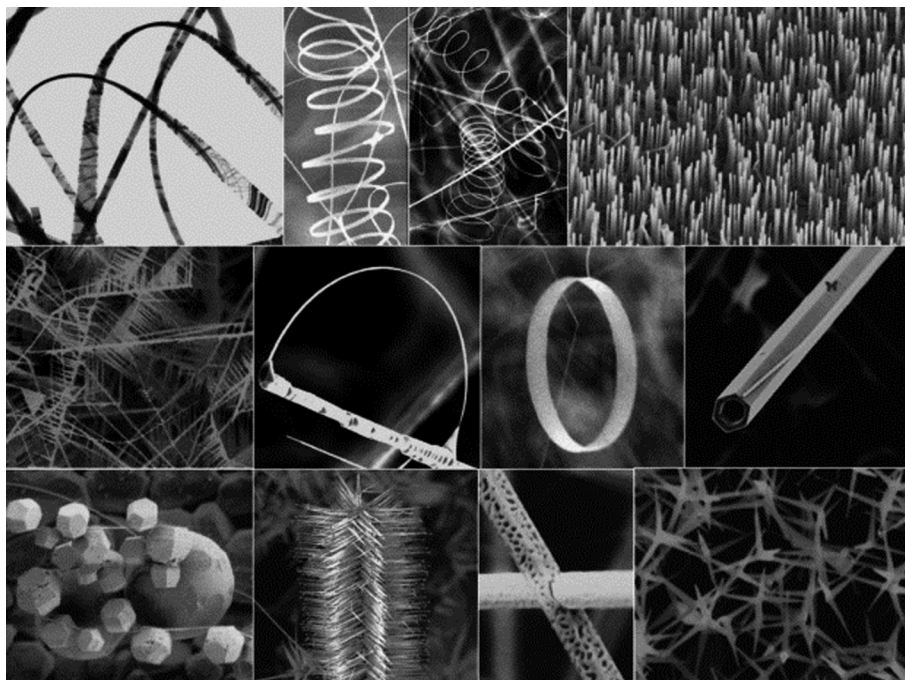


Figure 1.2 Nanostructured ZnO with different morphologies obtained by thermal evaporation of ZnO powders ([Wang, 2004a](#)).

1.2 Physical properties of ZnO

1.2.1 Crystal structure of ZnO

Crystal structure is a unique arrangement of atoms or molecules in a crystalline material, which plays an important role in determining the physical properties of a material, such as band structure and optical transparency. As a result, knowledge of the crystal structure of ZnO is essential to study the formation of different ZnO nanostructures.

ZnO crystallizes in two main crystal structures: hexagonal wurtzite and cubic zincblende, as shown in Figure 1.3(a) and (b). Wurtzite is the most stable crystal structure of ZnO under ambient conditions, which explains why hexagonal prism-shaped ZnO nanocrystals are most commonly observed. Zincblende ZnO is stable only by growth on substrate with cubic lattice structure. In addition to wurtzite and zincblende polymorphs, ZnO can be crystallized in the rock salt motif at relatively high pressures above 10 GPa (Figure 1.3(c)) (Morkoç & Özgür, 2008; Özgür et al., 2005).

In wurtzite and zincblende ZnO, both zinc and oxygen centers are arranged tetrahedrally, which is known as the characteristic geometry of Zn (II). The tetrahedral arrangement of ZnO leads to a noncentral symmetry and results in piezoelectricity for wurtzite and zincblende ZnO and pyroelectricity for wurtzite ZnO. The wurtzite structure of ZnO belongs to the space group of $P6_3mc$. The ratio of the lattice constants c/a for wurtzite ZnO is around 1.6 ($a = 0.3296$ nm and $c = 0.5207$ nm), which is very close to the ideal value of a hexagonal cell (1.633). The bonding in ZnO is mainly formed through the electrostatic attraction (ionic bonding) between Zn^{2+} and O^{2-} , where the radii of Zn^{2+} and O^{2-} are 0.074 nm and 0.14 nm, respectively. The ZnO bond has a considerable degree of polarity, which is caused by the very strong electronegativity of oxygen. The high bond polarity of ZnO makes the wurtzite structure more favorable as compared with the zincblende structure.

Because of the prominent bond polarity, the c -axis [0001] of ZnO has a pronounced polar character. ZnO (0001) surface can be positively or negatively charged, depending

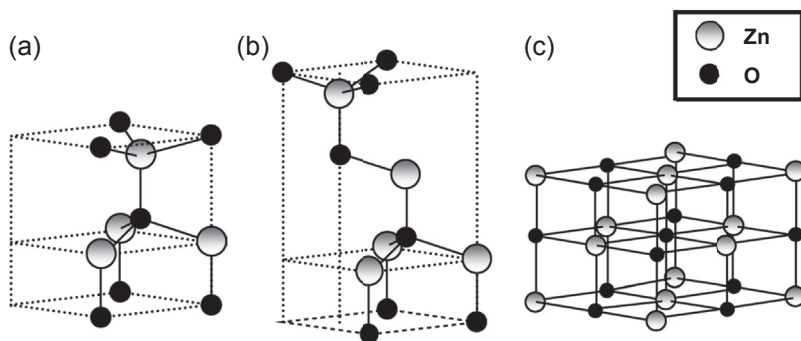


Figure 1.3 Ball-and-stick representations of ZnO crystal structures: (a) hexagonal wurtzite, (b) cubic zincblende, and (c) cubic rock salt (Morkoç & Özgür, 2008; Özgür et al., 2005).

on whether the surface is Zn^{2+} or O^{2-} terminated. Surface reconstruction usually occurs on crystal polar surfaces to maintain the surface stability and electrical neutrality, but it does not happen in ZnO. The (0001) surfaces of ZnO crystals are atomically flat, stable, and without surface reconstruction. Hexagonal wurtzite ZnO crystals grow along the c -axis, terminated with high-energy $\text{Zn}^{2+}/\text{O}^{2-}$ polar surfaces (Ye, Fang, Hao, Teng, & Zhang, 2005). During ZnO crystal growth, the precursor molecules tend to adsorb onto ZnO polar surfaces, as polar surfaces have higher surface energy. The polarity of the polar surfaces alternates after the adsorption of a new layer of precursor molecules, as the Zn^{2+} terminated surface is transformed into O^{2-} terminated surface, or vice versa (Xu & Wang, 2011). This process is repeated during ZnO crystallization, thus leading to a fast growth rate along the [0001] direction, which explains the formation of 1D ZnO nanostructures (Wang, 2004b).

1.2.2 Electrical properties of ZnO

ZnO is a direct bandgap semiconductor. At ambient conditions, ZnO has a relatively large bandgap of about 3.3–3.4 eV. By alloying with other metal oxides, like MgO and CdO, the bandgap of ZnO can be further enlarged to 4 eV. The large bandgap of ZnO makes it a material with superior features, such as low electronic noise, high breakdown voltage, and good stability under high temperature and large electric field conditions.

In its normal form, ZnO is an n-type semiconductor (conductivity by electrons). This conductivity is thought to be due to the existence of nonstoichiometric defects in the crystal lattice. However, some researchers have suggested another explanation based on theoretical calculations: the n-type characteristic of ZnO may originate from the accidental incorporation of hydrogen impurities (Look, Hemsley, & Sizelove, 1999; Janotti & Van deWalle, 2006). To strengthen the n-type doping of ZnO, we can either substitute zinc with Group III elements (such as Al, Ga, and In) or substitute oxygen with Group VII elements (such as Cl and I). Meanwhile, the p-type doping of ZnO still remains difficult, and this problem is caused by the poor solubility of p-type dopants as well as the compensation between p-type dopants and n-type impurities within the ZnO crystal lattice (Ohgaki et al., 2008). To date, Group I elements (such as Li, Na, and K) and Group V elements (such as N, P, and As) have been tried for preparing p-type ZnO, but many of these elements function as deep acceptors instead of introducing p-type conductivity under ambient conditions. Electron mobility of ZnO varies with temperature and reaches a maximum of $\sim 2000 \text{ cm}^2/(\text{V s})$ at -193.15°C (Wagner & Helbig, 1974). Reports on hole mobility of ZnO are still rare to date, with an estimated range between 5 and $\sim 30 \text{ cm}^2/(\text{V s})$. The exciton binding energy of ZnO is $\sim 60 \text{ meV}$ at 300 K, which is one of the reasons why ZnO is so attractive for optoelectronic applications.

Piezoelectric property has been observed in ZnO crystals. As mentioned in the previous section, ZnO crystal has noncentrosymmetric crystal structure, which is due to the tetrahedral arrangement of Zn^{2+} and O^{2-} centers. The noncentrosymmetry of ZnO results in piezoelectricity, caused by the polarization at atomic level. Under normal conditions, no dipole exists in ZnO crystals, as positively charged Zn^{2+} centers

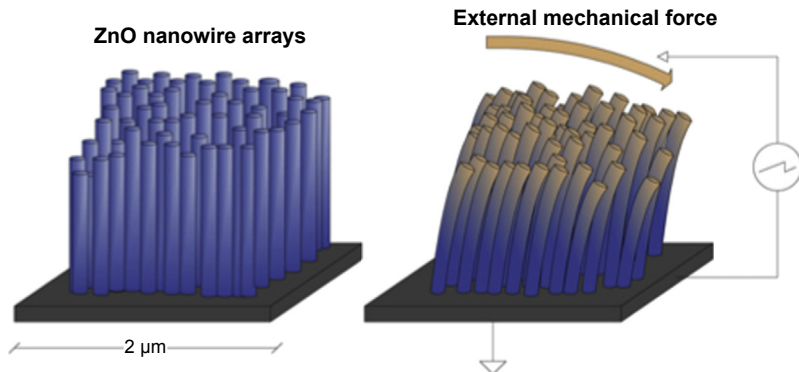


Figure 1.4 The piezoelectric effect of ZnO nanowire arrays upon the exertion of an external mechanical force (Akyildiz & Jornet, 2010).

and negatively charged O^{2-} centers compensate with each other. However, if an external force is applied onto the crystal, the Zn^{2+} and O^{2-} centers will be displaced from their initial positions, leading to the formation of an electric dipole. If a single-crystalline ZnO is subjected to an external force, the microscopic dipoles will line up along the same direction, resulting in the formation of macroscopic dipoles as shown in Figure 1.4 (Akyildiz & Jornet, 2010). Based on this property, scientists have successfully developed ZnO nanogenerators that may convert kinetic energy into electricity.

1.2.3 Optical properties of ZnO

ZnO is an excellent photonic material in the blue–UV region because of its large direct bandgap of 3.3–3.4 eV and large exciton binding energy of 60 meV. In recent studies, researchers have shown that ZnO can be used as a host matrix to incorporate rare earth and magnetic dopants, which makes ZnO a promising material for novel optical and optomagnetic applications. Owing to the quantum confinement effect, nanostructured ZnO usually exhibits enhanced optical properties, which have been intensively studied for applications in photonic or photoelectrical devices.

The photoluminescence spectra of different ZnO nanostructures, such as 1D ZnO nanowires and nanotubes, have been extensively studied (Li, Meng, Zhang, & Phillipp, 2000; Shalish, Temkin, & Narayanamurti, 2004; Xing et al., 2003). In general, two emission bands of ZnO triggered by different mechanisms can be observed under UV excitation (Xu & Wang, 2011). The band in the UV range is the near-band-edge emission caused by the collisions of photogenerated excitons (Lyu et al., 2002), while the one in the visible range is due to the recombination of electrons and holes at the deep level within the bandgap, due to the presence of various defects (Xu, Guo, Liao, Zhang, & Xu, 2005; Tam et al., 2006). As shown in Figure 1.5, most photoluminescence features of nanostructured ZnO are consistent with those of bulk ZnO, including the major emission peak at a wavelength of 380 nm due to the band transition and the continuous emission band from 450 to 600 nm (green–yellow region) caused by the oxygen

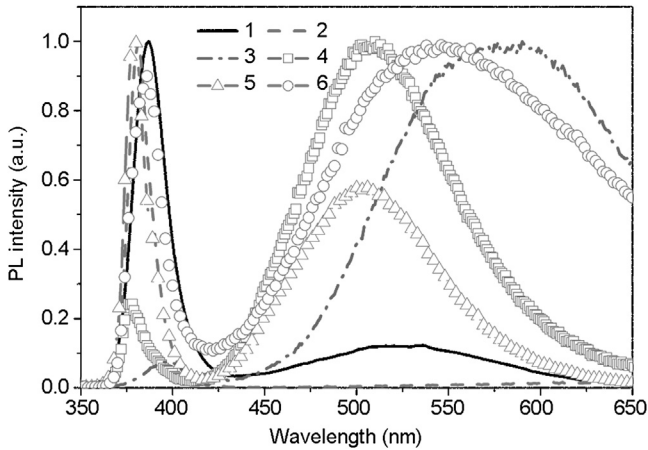


Figure 1.5 Photoluminescence spectra of different nanostructured ZnO at room temperature: (1) tetrapods, (2) needles, (3) nanorods, (4) shells, (5) well-aligned nanorods, and (6) nano-ribbons (Djurišić & Leung, 2006).

vacancy in the ZnO crystal lattice (Djurišić & Leung, 2006). It was found that the green emission intensity of ZnO nanowire arrays could be increased by reducing the diameter of nanowires. Some researchers have explained the science behind this observation—thinner nanowires possess much larger surface-to-volume ratios, resulting in more surface defects and recombinations, which could enhance the emission intensity of ZnO (Shalish et al., 2004; Yang et al., 2002). Fan et al. (2004) reported the green–red luminescence band of ZnO, which was attributed to native defects, like single- or double-ionized oxygen vacancies.

The study of photoluminescence indicates that 1D ZnO nanostructures are promising materials to be used in UV–blue range emission applications. The large refractive index and near-cylindrical structure make ZnO nanowires excellent candidates as optical waveguides. ZnO nanowires with flat polar surfaces can create optical resonance cavities, thus further enhancing the directional lasing performance at room temperature (Djurišić & Leung, 2006). The lasing power threshold of ZnO was reported in the range of 40–100 kW/cm², and a lower threshold could be achieved with higher-quality ZnO crystals. In addition, the quantum confinement effect in ZnO nanowire arrays yields a substantial density of states near the band edges, which could enhance the radioactive efficiency (Fan et al., 2004).

1.3 Methods for the preparation of 1D ZnO nanostructures

A variety of synthetic methodologies have been developed for the preparation of 1D ZnO nanostructures. Based on the synthesis medium, these methods can be generally categorized into two groups: vapor phase and solution phase methods. The vapor

phase method is the most extensively studied approach for growing 1D ZnO nanostructures. Numerous comprehensive reviews and book chapters have discussed the vapor phase growth of ZnO nanostructures. This section will focus on the solution phase method for growing 1D ZnO nanostructures.

1.3.1 Synthesis of suspended ZnO nanowires

Over the past few years, many solution-based synthesis methods have been developed for growing 1D ZnO nanowires. The solution method requires the understanding of the intrinsic crystal structure of ZnO and the ability to tune the growth rate of different crystal planes. Capping reagents are usually added during the synthesis to kinetically control the growth rates of various crystal planes to achieve anisotropic growth. For example, Liu and Zeng had successfully synthesized ZnO nanowires in the diameter regime of 50 nm using a hydrothermal method (Liu & Zeng, 2003). Figure 1.6 shows the typical XRD pattern and TEM images of the as-synthesized ZnO nanowires. In this particular synthesis, ethylenediamine was used as the capping ligand to confine the growth of ZnO nanowire along the c -axis. If the reaction temperature was lowered to room temperature, the resulting diameter and length of ZnO nanowires could be further reduced to less than 20 nm and more than 1 μm , respectively, resulting in exceptionally large aspect ratios in the range of 30–40 (Liu & Zeng, 2004a, b). By further tuning the pH of the growth

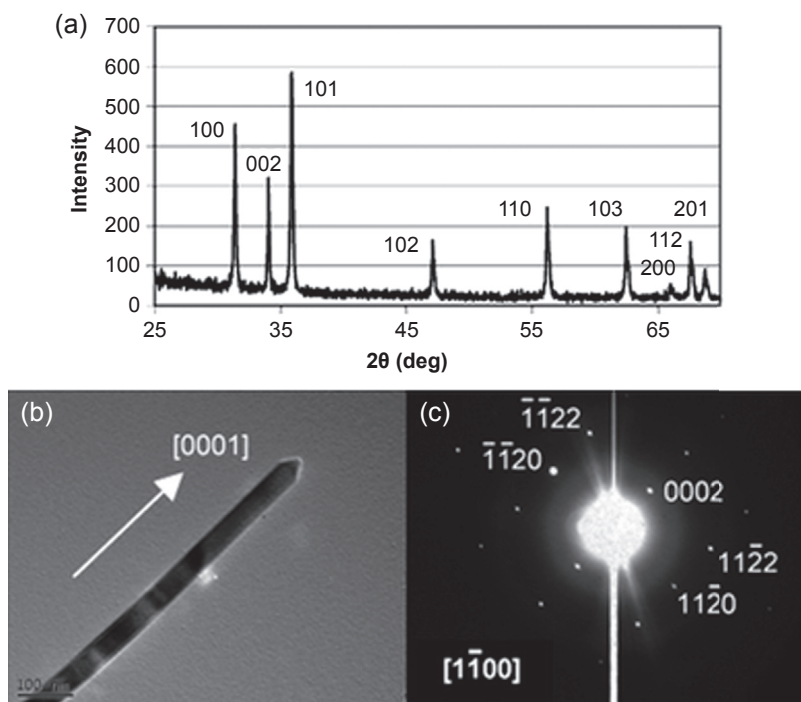


Figure 1.6 (a) XRD pattern of the as-prepared ZnO nanorods, (b) TEM image of a free-standing ZnO nanorod, and (c) SAED pattern of the nanorod in (b) (Liu & Zeng, 2003).

solution, hollow ZnO nanowires (i.e., nanotubes) could be obtained. Figure 1.7 shows a series of TEM images of single-crystalline ZnO nanotubes with uniform diameters (Liu & Zeng, 2009). The formation process of these enclosed ZnO nanotubes is schematically illustrated in Figure 1.8 (Liu & Zeng, 2009).

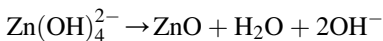
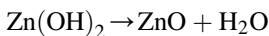
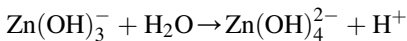
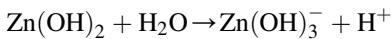
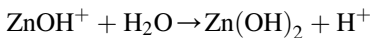
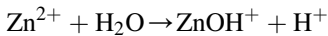
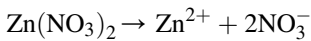
1D ZnO nanostructures can be used as building blocks to construct complex 3D hierarchical superstructures. Figures 1.9 and 1.10 show ZnO “dandelions” and hollow spheres made from 1D ZnO nanowires and nanorods (Liu & Zeng, 2004a, b, 2007).

1.3.2 Synthesis of ZnO nanowire arrays

ZnO nanowires can be synthesized as arrayed thin films on planar substrates by either seeded methods, such as hydrothermal synthesis and electrochemical deposition (Xu & Wang, 2011), or seedless growth techniques, such as van der Waals epitaxy (Utama et al., 2012; Zhu et al., 2013). These different synthetic strategies allow the successful deposition of ZnO nanowire arrays on a variety of substrates, such as transparent conductive oxides, metals, muscovite mica, and graphene.

To grow ZnO nanowire arrays on substrate using a seed-assisted solution chemical method, a two-step approach is generally used (see Figure 1.11). First, a very thin layer of ZnO nanocrystals is coated on the surface of the substrate. The ZnO nanocrystals act as the crystal seeds to lower the nucleation energy, thus promoting heterogeneous crystal growth. Then in the second step, 1D ZnO nanowires are grown on seeded substrates in a growth solution.

Zinc nitrate is frequently used as the zinc precursor for growing 1D ZnO nanowires. When dissolved in water, zinc nitrate immediately hydrolyzes to produce zinc hydroxyl species including ZnOH^+ , Zn(OH)_2 , Zn(OH)^- , Zn(OH)_4^{2-} , and Zn(OH)_3^- (Govender, Boyle, Kenway, & O'Brien, 2004). These species are in equilibrium with each other in the aqueous phase. Dehydration of zinc hydroxyl species leads to the formation of ZnO. The hydrolysis of zinc nitrate and dehydration of hydroxyl species are summarized in the following equations (Demianets & Kostomarov, 2001; Dem'yanets, Kostomarov, & Kuz'mina, 2002; Viswanatha, Amenitsch, & Sarma, 2007):



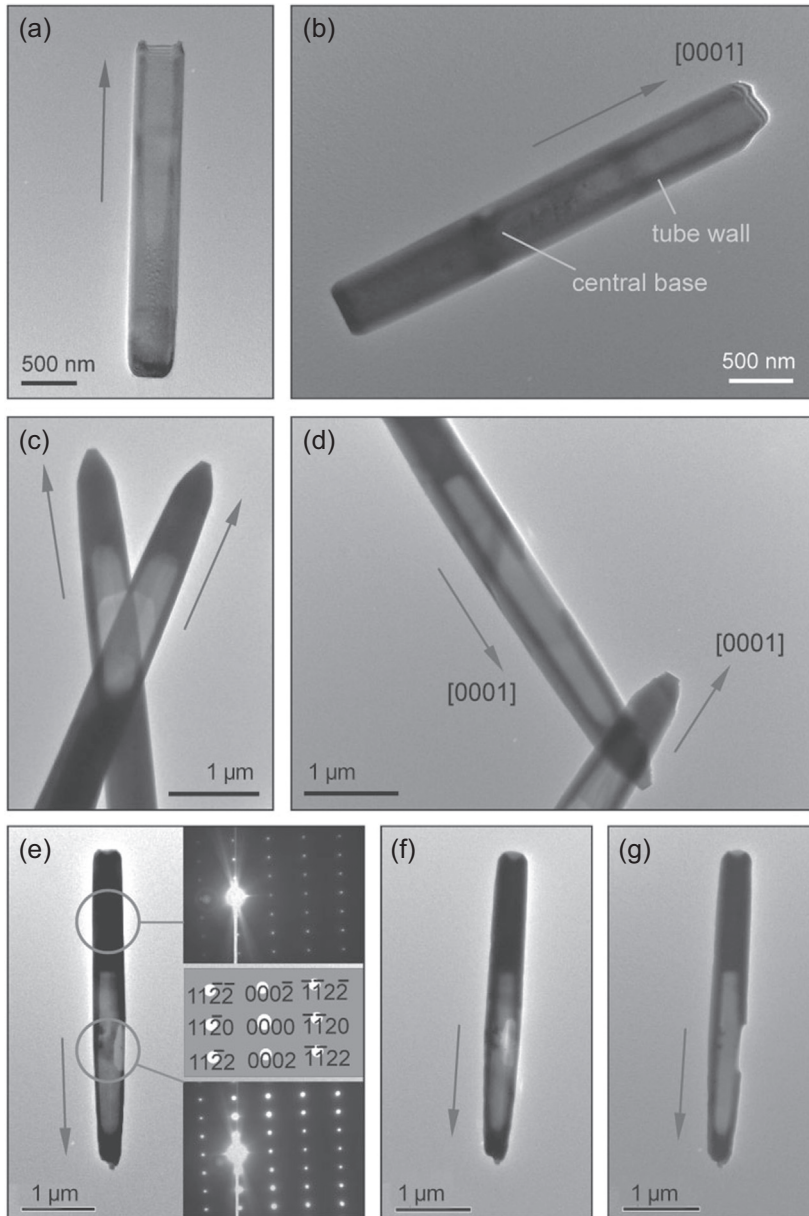


Figure 1.7 TEM images of ZnO nanotubes: (a), (b) two concave growing heads (open ends) of ZnO nanotubes; (c), (d) closed ZnO nanotubes after volume inversion; (e), (g) angle-dependent measurement for a closed ZnO nanotube ((e) 0° , (f) $+40^\circ$, (g) -40°). Two SAED patterns and their diffraction beam assignment, which corresponds to the $[1-100]$ zone spots of ZnO, are also displayed in (e) for the circled areas of the nanotube. In all cases, the arrows indicate the major growth direction $[0001]$ (Liu & Zeng, 2009).

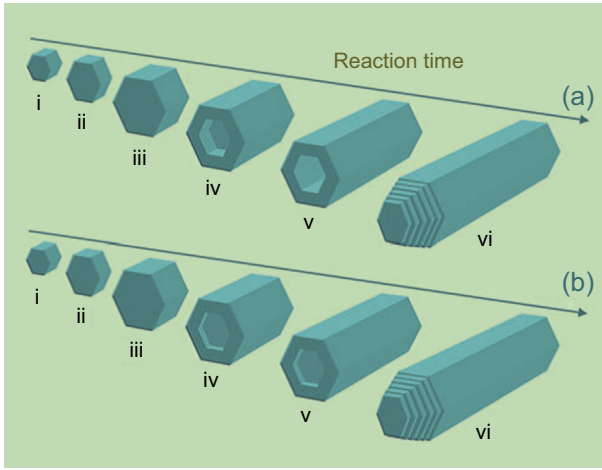


Figure 1.8 Schematic illustration of the formation of (a) ZnO nanotubes and (b) ZnO nanorods, depending on relative growth rates of the wall rim and the central base of the growing heads. In both cases, the volume inversion of the growing head (along the $[0001]$ direction) is depicted in stages iv–vi (Liu & Zeng, 2009).

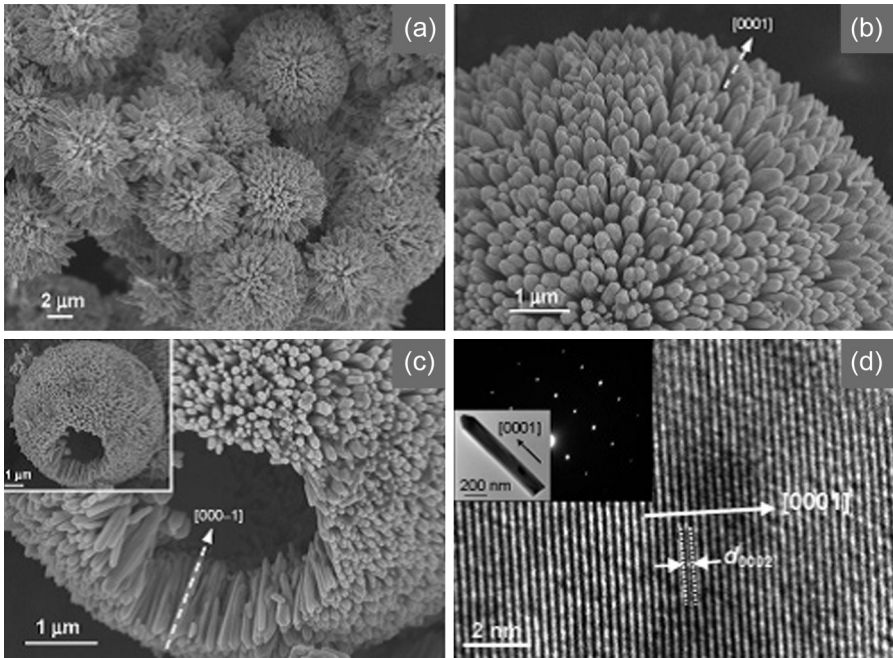


Figure 1.9 FESEM images (a–c) of ZnO dandelions. (a) Overall product morphology. (b, c, and inset) Detailed shell structures assembled by ZnO nanorods. (d) SAED (inset) and an HRTEM image (Liu & Zeng, 2007).

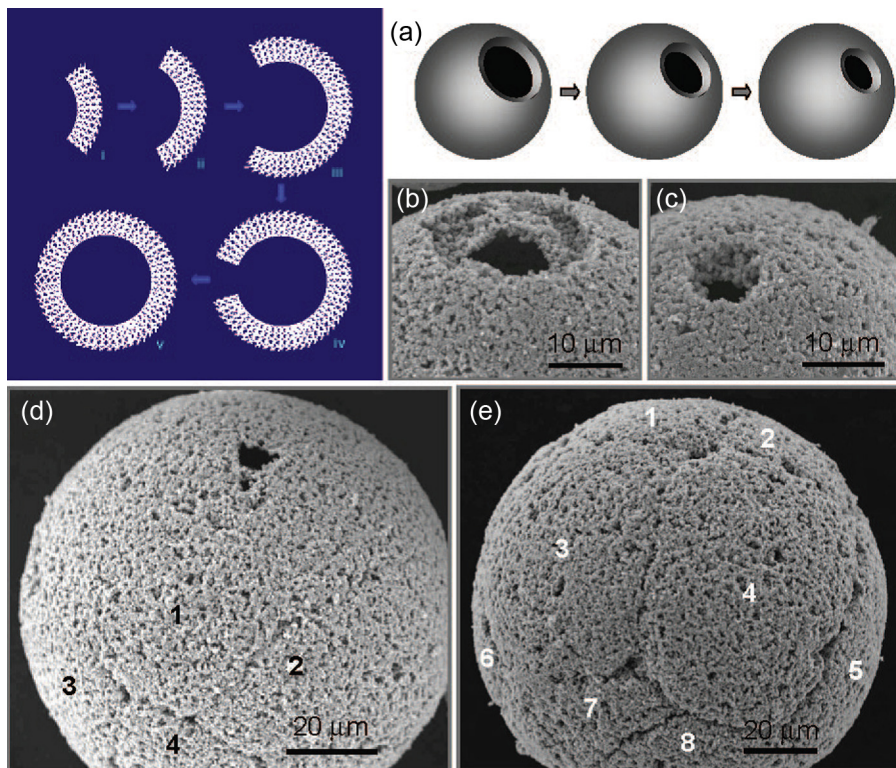


Figure 1.10 (a) Self-assembling process (see steps i–v of the color inset, cross-sectional view); (b, c) FESEM images of final openings of ZnO microspheres corresponding to (a); and (d, e) SEM images of domains (marked with alphabetical numbers) of assembled nanobuilding units (Liu & Zeng, 2007).

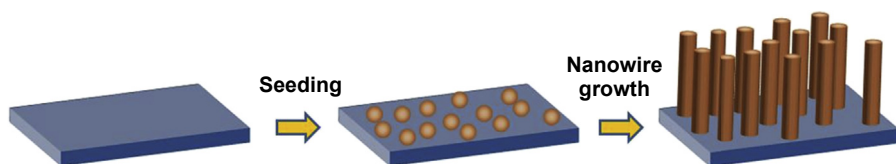


Figure 1.11 A two-step process for growing 1D ZnO nanowires on a substrate.

Reaction conditions would affect the preferential crystal growth direction of ZnO, thus resulting in the formation of a wide range of ZnO nanostructures. The formation of ZnO nanowires occurs when the pH of the precursor solution lies in between 5 and 12, at a temperature of 50–200 °C. If the pH of the precursor solution is greater than 9, the formation of ZnO nanowires can take place without any addition of additives. Otherwise, an additive such as hexamethylenetetramine (HMTA) is necessary to promote the growth of 1D ZnO nanostructures.

Well-aligned ZnO nanowire arrays could be easily grown on ZnO nanocrystal-seeded substrates using a hydrothermal approach (Tak & Yong, 2005; Greene et al., 2005). The seeding layers are crucial for ZnO nanowire array synthesis, as they not only act as nucleation sites for growing ZnO nanowires but also improve the contact between substrate and nanowires. Without seeding layers, the density of ZnO nanowires on substrate is very low and the nanowires grow in random directions. Over the past few years, various seeding methods have been developed, including atomic layer deposition, spin coating, dip coating, etc. (Yang, Zhao, & Willander, 2009; Li et al., 2005).

Solution-based electrochemical deposition can also be utilized to synthesize ZnO nanowire arrays, especially ZnO nanowire arrays in large areas on various conductive substrates (Xu et al., 2005). Electrochemical deposition of ZnO is usually conducted at low temperatures below 100 °C. The growth rate of ZnO could be greatly enhanced by applying an external potential, which accelerates the diffusion rate of the ionic precursor, and thus shortens the required deposition time for growing ZnO nanowires. For electrochemical ZnO nanowire growth, the most commonly used zinc precursor is zinc nitrate, which can react with water to produce excess hydroxyl groups—an essential component for ZnO growth. Typically, the concentration of $\text{Zn}(\text{NO}_3)_2$ used for ZnO deposition is about 5 mM, with 50 mM of NaNO_3 as the electrolyte.

1.4 Applications of 1D ZnO nanostructures

Owing to their unique chemical and physical properties, 1D ZnO nanostructures have been extensively studied and applied in various applications, including sensors, nanoelectronics, optics, energy harvesting devices, etc. In this section, we will discuss the application of 1D ZnO nanostructures in solar energy harvesting devices and sensors.

1.4.1 Solar cells

Solar cells, or photovoltaic cells, are electrical devices that convert solar energy directly into electricity through the photovoltaic effect. The basic working principle of a solar cell involves the generation of charge carriers upon illumination, the separation of charge carriers, and the transportation of charge carriers to the external circuit. Up to now, most solar cells have been based on the solid-state p–n junction, mainly constituted by crystalline silicon (c-Si), benefiting from mature semiconductor technology. However, high manufacturing costs are necessary to produce and process high-quality silicon solar cells. In addition, relatively thick silicon crystals are needed to maximize the capture of solar irradiation, due to the low light-scattering capability and poor light absorption of silicon. Due to these limitations, the cost of power supply by silicon solar cells is still not comparable to that from fossil fuels. Under these circumstances, scientists are seeking alternative solutions to substitute conventional silicon-based solar cells, leading to the emergence of new-generation excitonic solar

cells, such as dye-sensitized solar cells (DSCs), organic solar cells (OSCs), and hybrid solar cells (HSCs). 1D ZnO nanostructures are promising candidates for excitonic solar cells because of their low reflectivity, large surface area, and enhanced charge collection efficiency (Xu & Wang, 2011; Gonzalez-Valls & Lira-Cantu, 2009; Zhang, Dandeneau, Zhou, & Cao, 2009).

DSCs are different from conventional p–n junction solar cells. In a DSC, the light absorption and charge carrier transport are decoupled into two different materials. The basic working principle of a DSC is shown in Figure 1.12 (Grätzel, 2001). In these devices, dye molecules are excited from ground state to excited state upon the absorption of incident photons, leading to the injection of photogenerated electrons into the conduction band of an adjacent oxide semiconductor. The electrons are then transported to the counterelectrode through the external circuit, where useful work can be done. The original state of the dye is subsequently restored by electron donation from the redox couple (e.g., iodine/triiodide), while iodide is regenerated by the reduction of triiodide at the counterelectrode. The utilization of a mesoporous titanium dioxide (TiO_2) electrode, with a high internal surface area, to support the monolayer adsorbed sensitizer significantly improved the performance of DSCs (O’regan & Grätzel, 1991). To date, TiO_2 nanoparticles are still the most popular choice among the many other candidates for DSCs. However, the lifetime and diffusion length of electrons need to be significantly improved to further enhance the DSC performance, as electrons have to percolate the networks consisting of sintered TiO_2 nanoparticles, where trap-limited interparticle hopping events take place (Benkstein, Kopidakis, Van de Lagemaat, & Frank, 2003).

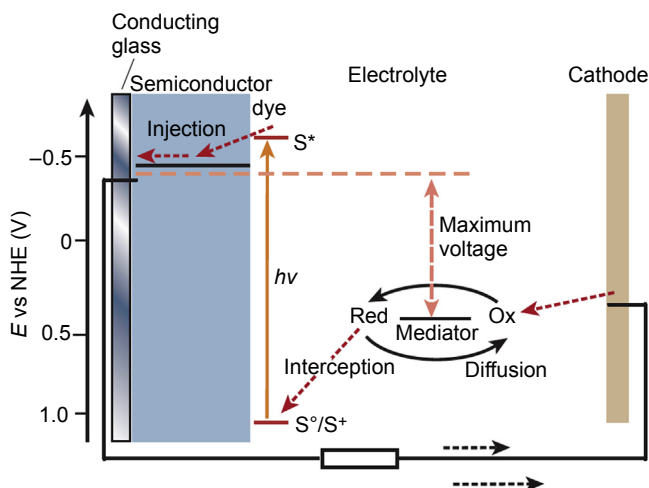


Figure 1.12 Schematic illustration of the working principle and electron transfer process in dye-sensitized solar cells. Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of a semiconductor film. Dye molecules are regenerated by the redox system, in which they are regenerated at the counterelectrode by electrons passed through the external circuit. Potentials are referred to the normal hydrogen electrode (NHE) (Grätzel, 2001).

To overcome the intrinsic disadvantages of TiO_2 nanoparticles for charge transport in DSCs, great efforts have been devoted to the development of 1D semiconductor nanostructures (Baxter & Aydil, 2005; Feng et al., 2008; Law, Greene, Johnson, Saykally, & Yang, 2005; Liu & Aydil, 2009; Martinson, Elam, Hupp, & Pellin, 2007; Mor, Shankar, Paulose, Varghese, & Grimes, 2006; Zhu, Neale, Miedaner, & Frank, 2007) as 1D semiconductor nanostructures are believed to offer direct transport pathways for photogenerated electrons, which can greatly shorten the electron diffusion distances, thus contributing to better electron collection efficiency for DSCs (Baxter & Aydil, 2005; Beermann, Vayssieres, Lindquist, & Hagfeldt, 2000). The high crystallinity along with the reduced number of grain boundaries and surface defects of 1D nanostructures can accelerate electron transport, hence reducing the possibility of interfacial charge recombination (Mor et al., 2006; Zhu et al., 2007). Based on these attractive properties, Yang et al. first demonstrated the use of ZnO nanowire arrays as a photoelectrode in DSCs (Figure 1.13) (Law et al., 2005). In Yang's work, dense ZnO nanowire arrays were grown on FTO substrates in an aqueous environment through a two-step seeded growth approach. The aspect ratio

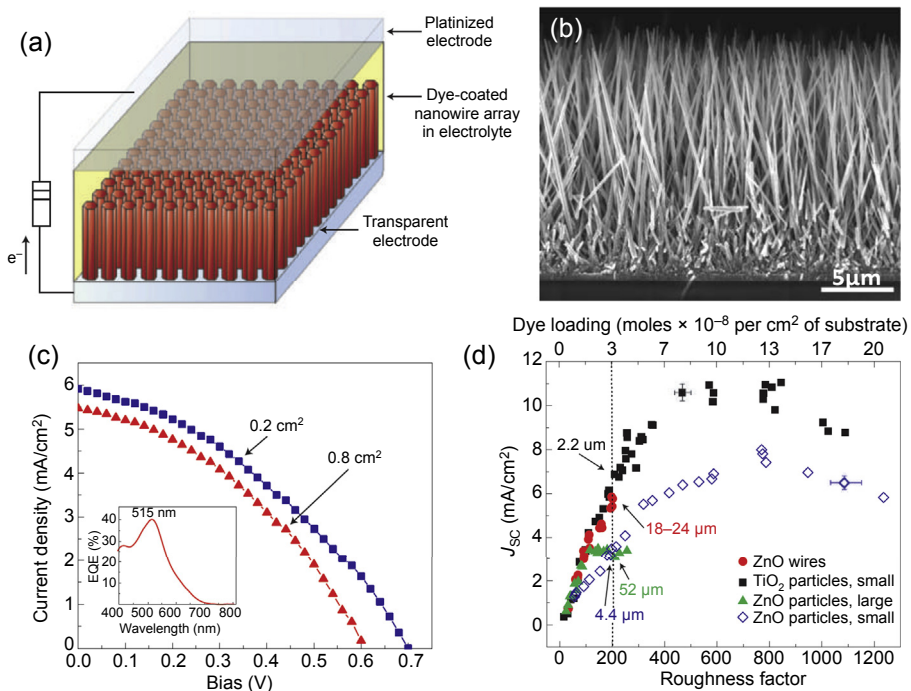


Figure 1.13 (a) Schematic illustration of ZnO nanowire-based DSCs. (b) Typical cross-sectional SEM image of ZnO nanowire arrays on FTO substrate. (c) Photocurrent density against voltage plots of two ZnO nanowire-based DSCs with different sizes but the same roughness factor. (d) The short-circuit current density against roughness factor plots for DSCs fabricated using ZnO nanowires, TiO_2 nanoparticles, and ZnO nanoparticles (Law, Greene, Johnson, Saykally, & Yang, 2005).

(the ratio of height to diameter) of the ZnO nanowires was boosted to greater than 125 by adding polyethylenimine (PEI). The ZnO nanowires exhibit excellent conductivity along the vertical direction, with a measured resistivity of 0.3–2.0 Ω cm. However, compared to TiO₂ nanoparticle photoelectrodes used in DSCs, the inadequate surface area of 1D ZnO nanowire film significantly limits the dye adsorption capacity, making the ZnO nanowire-based DSCs less efficient as compared with TiO₂ nanoparticle-based DSCs.

1.4.2 Water splitting cells

Besides the development of solar cell technologies, the scientific community is also studying moving from an oil-based economy to a hydrogen-based economy. Hydrogen gas possesses an energy density of 123 MJ/kg, which is much larger than the values of gasoline (47.2 MJ/kg) and coal (24 MJ/kg). Combustion of hydrogen produces water, which has no impact at all on the environment. Worldwide, the earth receives an average energy influx of 1.61 kW/m² from the sun; meanwhile, water covers 70.9% of the earth's surface. Based on these facts, it is anticipated that the combination of these two abundant natural resources should serve as part of the solution to our energy issues.

Semiconductor metal oxides, such as ZnO and TiO₂, have been extensively studied as photoelectrodes for water splitting applications to produce hydrogen (Fujishima, 1972). Compared with TiO₂, ZnO possesses a 10–100-fold higher electron mobility (Hendry, Koeberg, O'Regan, & Bonn, 2006), making it a more popular choice of material for photoelectrochemical applications. However, because of the wide bandgap nature of ZnO, the power conversion efficiency of pure ZnO is limited by its poor visible light absorption. In this case, doping and sensitization are effective strategies to further enhance the photoelectrochemical activities of 1D ZnO nanostructures.

Yang et al. (2009) reported a rational synthesis of nitrogen-doped ZnO nanowire arrays (ZnO:N) and studied their applications as photoanodes for photoelectrochemical hydrogen generation. The uniform and well-aligned ZnO nanowires were prepared using a hydrothermal approach, followed by an annealing process in ammonia to incorporate nitrogen as a dopant. The ZnO:N nanowire arrays showed enhanced photoresponse within the visible light region, as the incorporation of nitrogen could introduce intermediate energy levels in the bandgap of ZnO, thus leading to a redshift of the absorption spectrum of ZnO. Compared to the pristine ZnO nanowires synthesized under similar conditions, the ZnO:N nanowires demonstrated increased photocurrent density (Figure 1.14) and photo-to-hydrogen conversion efficiency.

Quantum dot (QD) sensitization is another effective way to extend the photoresponse of pristine ZnO to the visible solar spectrum. Many different types of narrow bandgap semiconductor QDs, such as CdS (Lee, Min, Dhas, Ogale, & Han, 2009), CdSe (Miao, Yang, Khoo, & Liu, 2013; Leschkes et al., 2007), and CdTe (Chen et al., 2010; Wang et al., 2010), have been studied to sensitize various ZnO nanostructures. The modifications of QDs could remarkably enhance the overall energy conversion efficiency in photoelectrochemical devices, owing to the favorable

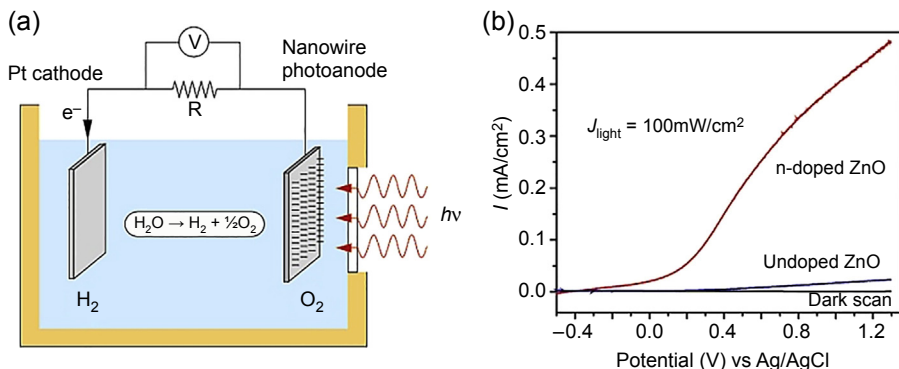


Figure 1.14 (a) Working principles of a nanowire-based photoelectrochemical water splitting device, with ZnO nanowires as the photoanode and Pt plate as the cathode. (b) Linear sweep voltammograms, collected at a scan rate of 10 mV/s at applied potentials from -0.5 to $+1.3$ V from undoped ZnO nanowires in the dark (black line), undoped ZnO nanowires, and 3.7% ZnO: N nanowires (red line) at 100 mW/cm^2 (Yang et al., 2009).

visible light absorption and tunable band structures of QDs. In general, QD sensitization can be accomplished by two major strategies. The first one involves direct growth of QDs on the surface of metal oxide electrodes using chemical bath deposition, electrochemical deposition, or successive ionic layer adsorption and reaction. For the second strategy, presynthesized colloidal QDs can be coated onto the metal oxide surface through direct adsorption or linker-assisted adsorption.

Chen et al. (2010) sensitized ZnO nanowires with CdTe QDs and applied them as photoelectrodes in nonsacrificial electrolyte for water splitting. Figure 1.15(a) shows a schematic illustration of the ZnO nanowire photoelectrode decorated with CdTe QDs and the charge-transfer mechanisms under illuminated conditions. ZnO nanowires with a length of $\sim 4 \mu\text{m}$ and a diameter of $\sim 150 \text{ nm}$, as shown in Figure 1.15(b), were synthesized using a modified hydrothermal method. The photoelectrochemical studies were carried out in a 0.5 M aqueous solution of Na_2SO_4 without any sacrificial reagents. The CdTe QD-sensitized ZnO nanowires demonstrate excellent photoresponses as well as good stability under light illumination. The outstanding performance of the CdTe-sensitized ZnO nanowires was attributed to the efficient photogenerated electron transfer from CdTe QD to ZnO nanowire, which greatly reduces the anodic decomposition and corrosion, thus leading to an improved stability of the device.

To further maximize the solar light absorption, tandem structures, in which semiconductors with different bandgap energies are combined to form optimum band structure, were developed and utilized in photoelectrochemical devices. Wang, Yang, Qian, Zhang, and Li (2010) reported that the fabrication of novel photoanodes consisted of double-sided CdS and CdSe QD-cosensitized ZnO nanowire arrays for PEC hydrogen generation. ZnO nanowire arrays were first grown on both sides of ITO-coated glass substrate using the hydrothermal approach, after which CdS and CdSe QDs were sequentially deposited onto ZnO nanowires using chemical bath deposition (Figure 1.16). The cosensitized photoelectrode shows significantly enhanced visible

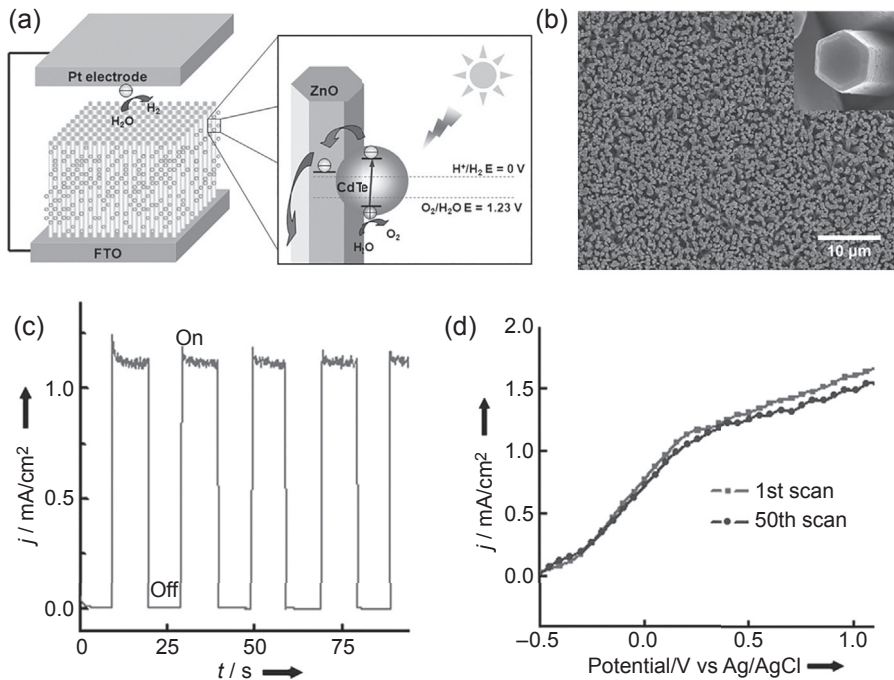


Figure 1.15 (a) Schematic illustration of ZnO nanowire arrays coated with CdTe and charge-transfer mechanisms. (b) SEM images of pristine ZnO nanowire arrays with high surface density. (c) Photocurrent responses of ZnO nanowires with/without CdTe QDs at 100 mW/cm² with on–off cycles. (d) Stability of PEC performance after 50 scans (Chen et al., 2010).

light absorption up to 650 nm. Both CdS and CdSe QDs possess conduction band edges higher than that of ZnO, thus leading to the efficient transfer of photogenerated electrons from QDs to ZnO. The photoelectrochemical measurements were carried out in a three-electrode setup, using coiled Pt wire and Ag/AgCl electrode as the counter- and reference electrodes, respectively. The electrolyte contains 0.25 M Na₂S and 0.35 M Na₂SO₃, which acts as a sacrificial reagent to prevent CdS and CdSe from photocorrosion. As shown in Figure 1.16(c), the double-sided CdS and CdSe QD-cosensitized ZnO nanowire arrays can generate a pronounced photocurrent density of ~ 12 mA/cm² at 0.4 V versus Ag/AgCl, which is twice the values of samples sensitized with a single type of QDs. Incident-photon-to-current measurements were performed to quantitatively probe the photoactivity of different photoanodes, and the cosensitized CdS–ZnO–ZnO–CdSe photoanode yields an almost constant IPCE of about 45% within the whole visible light region (400–650 nm), which is overwhelmingly better than other samples. The pronounced performance of this unique photoanode is mainly attributed to the integration of the advantage of QD sensitization and tandem cell configuration, which simultaneously enhanced the charge carrier collection and visible light absorption.

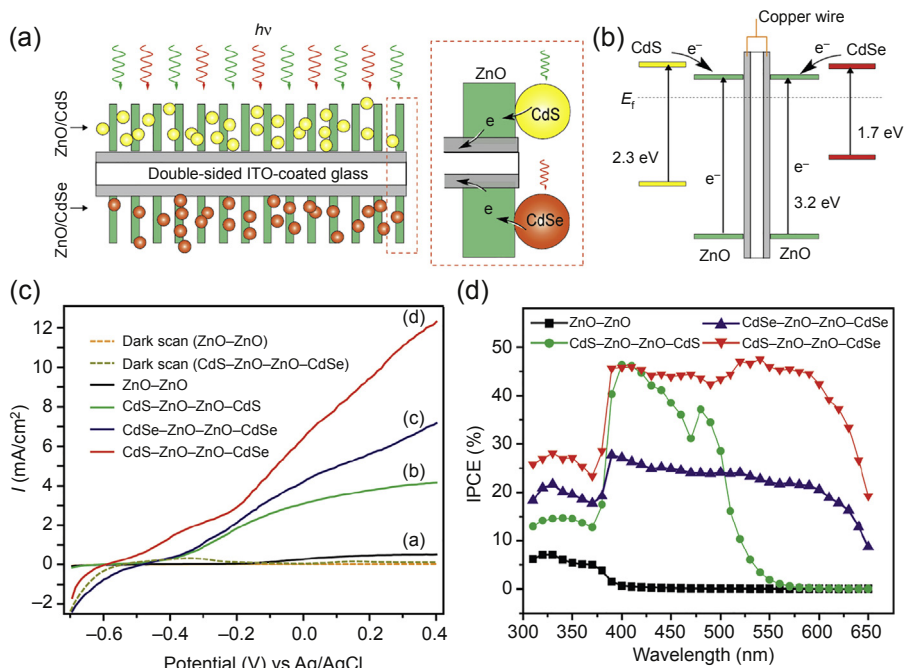


Figure 1.16 (a) Schematic illustration of the architecture of double-sided CdS–ZnO–ZnO–CdSe nanowire arrayed photoanode and (b) the corresponding energy diagram. (c) LSV curves of double-sided nanowire samples at a scan rate of 10 mV/s at applied potentials from -0.7 to $+0.4$ V, under 100 mW/cm^2 illumination. (d) The IPCE spectra of double-sided nanowire samples obtained with an incident wavelength of 310–650 nm at 0 V versus Ag/AgCl (Wang, Yang, Qian, Zhang, & Li, 2010).

As discussed previously, QD sensitization can be accomplished through different approaches, from chemical bath deposition to linker-assisted adsorption. Among the many different strategies, electrochemical deposition, which is cheap, simple, efficient, and scalable, is an attractive method for depositing semiconductor QDs. Recently, Miao et al. (2013) reported a facile all-electrochemical approach for the fabrication of arrayed ZnO–CdSe core–shell nanorods for efficient photoelectrochemical water splitting. In this work, both the ZnO nanorods core and the CdSe QDs shell were electrochemically deposited on ITO-coated glass substrates (Figure 1.17(a)). SEM images of the ZnO–CdSe core–shell nanorod arrays show that the CdSe nanocrystals are homogeneously distributed along the entire surface of ZnO nanorods, forming a uniform and dense outer shell (Figure 1.17(b)). The X-ray diffraction analysis indicates that the organic phase-based CdSe deposition did not affect the crystalline structure of ZnO nanorods. The thickness of the shell can be well tuned through controlling the CdSe deposition duration. In the photoelectrochemical tests, the optimized ZnO–CdSe nanorod arrays can generate a promising photocurrent density of 14.9 mA/cm^2 in $0.2 \text{ M Na}_2\text{S}$. Compared to undecorated ZnO nanorod arrays, the ZnO–CdSe nanorods

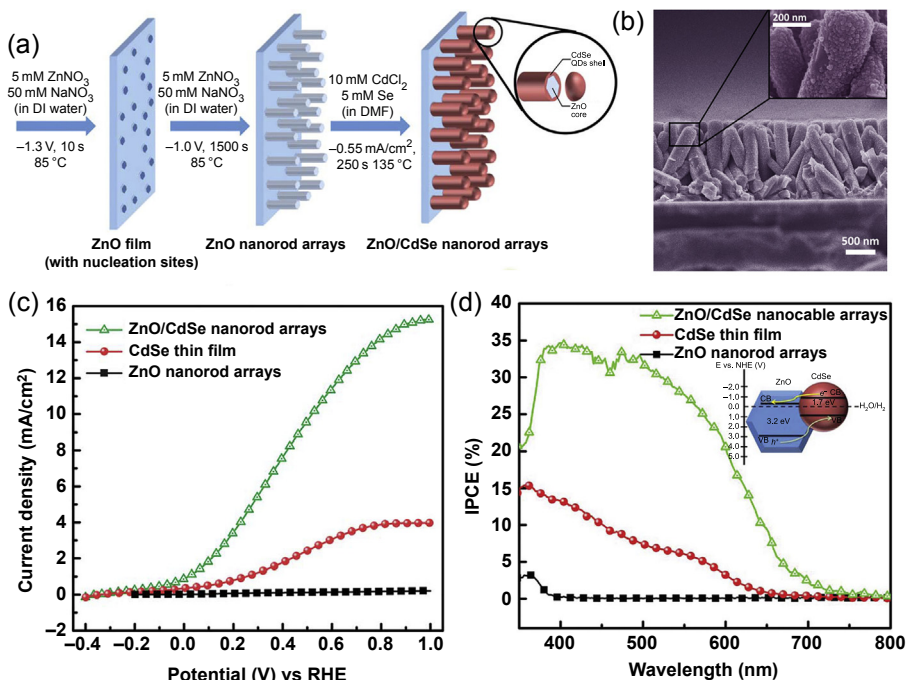


Figure 1.17 (a) Schematic illustration for the fabrication of ZnO–CdSe core–shell nanorod arrays through an all-electrochemical deposition approach. (b) Cross-sectional view FESEM images of ZnO–CdS nanorod arrays. (c) Linear sweep voltammograms and (d) IPCE spectra of ZnO–CdSe nanorod arrays, CdSe film, and ZnO nanorod arrays (Miao, Yang, Khoo, & Liu, 2013).

exhibit a significantly enhanced photoresponse within the visible light region, reaching a maximum IPCE value of $\sim 34.9\%$ (Figure 1.17(c)).

Apart from photoelectrochemical-based water splitting devices, ZnO nanowires were also studied as photocatalysts in suspended aqueous medium for water splitting. For example, Wang et al. (2010b) synthesized ZnO–CdS hybrid nanorods as an efficient photocatalyst, which showed stable long-term hydrogen generation under simulated solar illumination. Hong, Xu, Konishi, and Li (2010) proposed a different approach to split water based on the piezoelectrochemical properties of ZnO nanowires in which BaTiO₃ dendrite-decorated ZnO microfibers split water into H₂ and O₂ with a stoichiometric ratio of 2:1 under ultrasonic vibrations.

1.4.3 Sensors

Besides energy harvesting devices, 1D ZnO nanostructures have also been increasingly used in sensor applications, based either on the conductivity/piezoresistance change or the barrier height change at the contact, or on the p–n junction (heterostructured) diodes.

Seiyama, Kato, Fujiishi, and Nagatani (1962) observed that reactive gases such as carbon dioxide, benzene, and ethyl alcohol could induce significant changes in

electrical conductivity of ZnO films, due to electron donation from the reactive gas to the n-type ZnO film. Since then, numerous reports based on different ZnO nanostructures as gas sensors have been published. Wan et al. (2004) fabricated ZnO nanowire-based gas sensors with microelectromechanical system (MEMS) technology, as shown in Figure 1.18. As illustrated in Figure 1.18(b), when ZnO nanowires are exposed in air, oxygen molecules adsorb onto the surface of ZnO nanowires and capture electrons from the ZnO conduction band to form O_2^- ions, which increases the electrical resistance of ZnO. At moderate temperatures, reactive gases, for instance, ethanol, can react with the adsorbed oxygen species, which increases the electron concentration in ZnO, leading to the reduction of ZnO electrical resistance. Figure 1.18(d) shows the response and recovery of the resistance of ZnO nanowires when they are exposed to ethanol with different concentrations, from 1 to 200 ppm. The nanowire sensor showed a clear and rapid response at a very low ethanol concentration of 1 ppm. The sensitivity (S_g), defined as R_a/R_s , where R_a is the electrical resistance in air and R_s is the electrical resistance in ethanol and air mixture, increased with increasing ethanol concentration, with measured values of 47 and 1.9 at 200 and 1 ppm ethanol gas exposure. The outstanding sensitivity is attributed to the large surface-to-volume ratio of the ZnO nanowires. Based on similar working principles, 1D ZnO nanostructures have been integrated in different sensors to detect H_2 (Rout, Hari Krishna, Vivekchand, Govindaraj, & Rao, 2006), NO_2 (Ahn et al., 2008; Oh et al., 2009), and CO (Chang, Hsueh, Chen, & Huang, 2008).

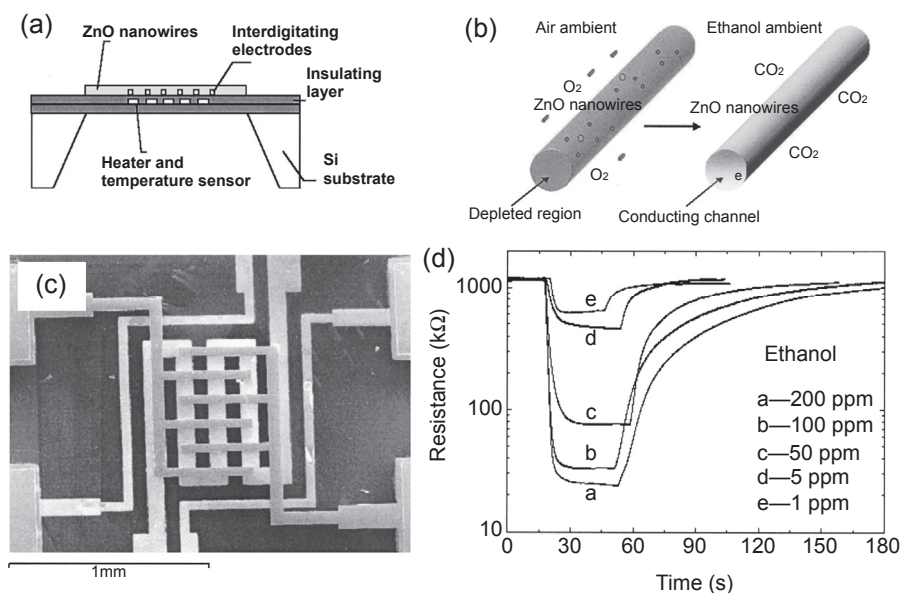


Figure 1.18 (a) Schematic illustration of a 1D ZnO nanowire-based gas sensor. (b) The working principle of a ZnO gas sensor to ethanol. (c) Top-view SEM image of the ZnO nanowire ethanol sensor. (d) The response–recovery characteristics of ZnO nanowires upon exposure to ethanol at 300 °C, with concentration from 1 to 200 ppm (Chen et al., 2010).

It is generally accepted that 1D ZnO nanomaterials are nontoxic and biocompatible at low concentrations (Zhou, Xu, & Wang, 2006; Li et al., 2008), which makes them ideal candidates for biological applications, for instance, biosensors. ZnO is an amphoteric oxide with isoelectric point (IEP) around 9.5 (Zang et al., 2007). In solutions, the surface of ZnO can be functionalized with either protons (H^+) or hydroxyl groups. By utilizing this property, Al-Hilli, Willander, Öst, and Strålfors (2007) studied ZnO nanorods as an intracellular sensor to measure the pH of living human adipocyte. In their experiments, ZnO nanorods were grown on the tips of silver-coated borosilicate glass capillaries using a low-temperature approach (Figure 1.19(a)). The variation in pH changes the surface charge of ZnO nanorods during protonation or deprotonation, which reflects as a voltage change detectable using voltmeters. Figure 1.19(b) shows the electrochemical potential difference of ZnO nanorods, which is linearly proportional to the change of pH in buffer solution in the pH range of 4–11 with sensitivity around 52 mV/pH. The experimental setup is schematically illustrated in Figure 1.19(c), in which a ZnO nanorod-decorated glass tip and a Ag/AgCl microelectrode were used as the working and reference electrodes, respectively; and the potential

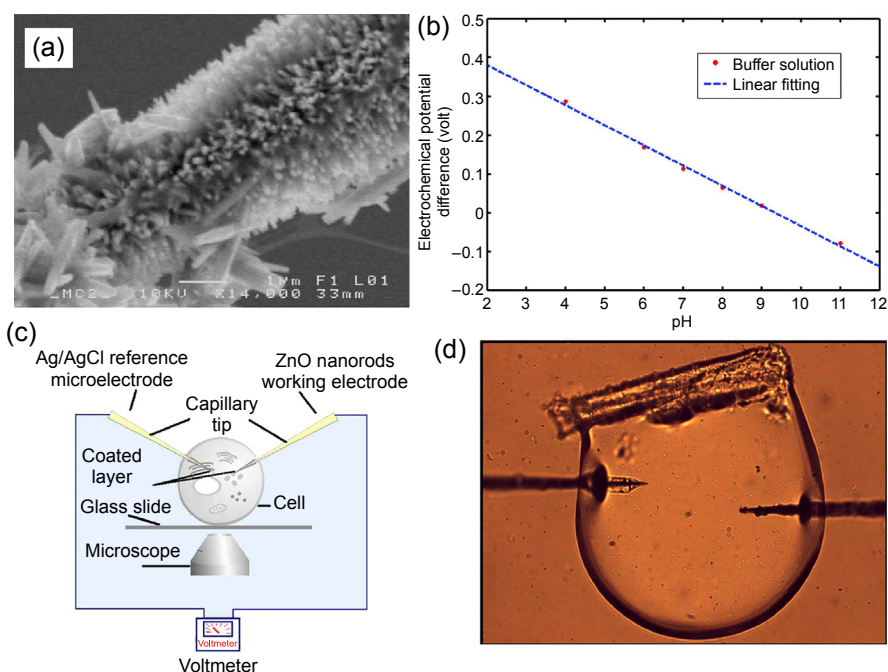


Figure 1.19 (a) The SEM image of the ZnO nanorod arrays grown on a silver-coated capillary using the low-temperature approach. (b) The electrochemical potential difference of ZnO nanorods versus pH changes curve for buffer solutions. (c) The schematic illustration of the intracellular pH measurements using ZnO nanorods and Ag/AgCl as the working and reference electrodes. (d) The optical microscopic image of the pH measurement performed on a human fat cell (Al-Hilli, Willander, Öst, & Strålfors, 2007).

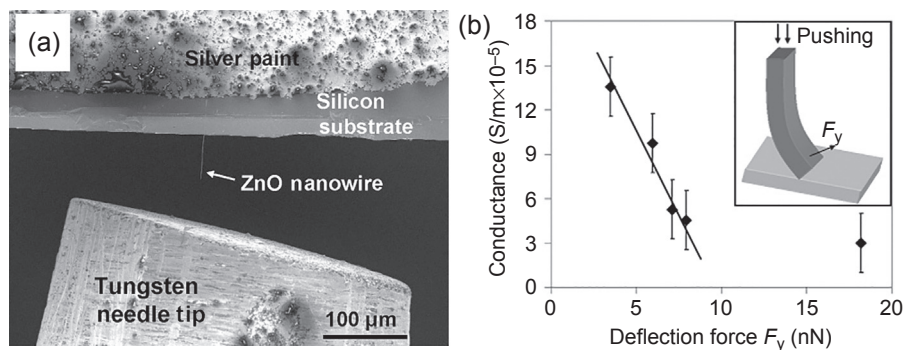


Figure 1.20 (a) SEM image shows the experimental setup for the nanoforce measurements using a ZnO nanowire. (b) The relationship between the conductance of the ZnO nanowire and the exerted deflection force obtained from experimental data (Wang & Song, 2006).

differences between the working and reference electrodes were monitored using a voltmeter. Figure 1.19(d) shows the optical microscopic image of the pH measurement performed on a living adipocyte—two electrodes penetrate the cell membrane and contact with the cytoplasm directly for the in situ measurement.

ZnO are positively charged due to protonation at the physiological pH range (7.3–7.4), allowing the spontaneous adsorption of biological functional groups with lower IEPs while retaining the biocompatibility. Based on this, 1D ZnO-based biosensors have been designed and developed to detect glucose (Zang et al., 2007; Wei et al., 2006; Wang et al., 2006; Kong et al., 2009), uric acid (Zhang et al., 2004), phenol (Gu et al., 2008; Zhao, Wu, & Zhi, 2009), and many other compounds.

As discussed previously, 1D ZnO nanostructures possess a unique piezoelectric property due to their noncentrosymmetric arrangements of Zn^{2+} and O^{2-} centers. Based on the piezoelectric property, Wang et al. (2010a) developed a 1D ZnO-based piezoelectric field effect transistor, which can function as a nanoforce/nanopressure sensor, by utilizing the coupled semiconducting and piezoelectric properties of ZnO (Figure 1.20).

1.5 Conclusion

For centuries, ZnO has played important roles in our daily lives, from bottled sunscreens to additives used in making rubber. Now thanks to the booming of nanotechnology in the past few decades, various nanostructures of ZnO have been designed and actualized for diversified purposes.

In this chapter, we have mainly discussed the properties, synthetic strategies, and potential applications of 1D ZnO nanostructures. These magical materials can be readily prepared through wet-chemical approaches such as hydrothermal synthesis and electrochemical deposition, which are safe, efficient, cost-effective, and scalable.

Owing to their unique crystal structures, superior electrical, optical properties, and excellent biocompatibility, the utilization of these 1D ZnO nanostructures has been demonstrated in numerous novel applications, including solar cells, solar water splitting, sensors, and many others. Although bold and encouraging progress has been made in recent years, there are still many issues to be addressed before we can apply 1D ZnO nanostructures to practical commercial and industrial applications.

It is still too early to draw final conclusions about the future of 1D ZnO nanostructures, but we believe that these fascinating nanobuilding blocks have great future potential.

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II–VI compound semiconductor nanowires: Optical properties and nanophotonics

2

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2.1 Introduction

Since the observation of phosphorescence from ZnS crystals in 1866, group II–VI semiconductors have been intensively studied, especially since the 1920s (Chadi, 1994). Over the past two decades, group II–VI compound semiconductor nanowires, benefiting from the continued success and rapid development of nanotechnology, have attracted much attention for the development of novel optoelectronic devices, attributed to their excellent optical and electric properties superior to bulk counterparts (Fang & Zhang, 2006; Fang, Wu, & Hu, 2011; Jie, Zhang, Bello, Lee, & Lee, 2010; Kar & Chaudhuri, 2006; Utama et al., 2012b; Wang, 2004; Yang et al., 2002; Zhai, Fang, Li, & Golberg, 2010). The rich family of group II–VI semiconductors (including ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe) generally covers the whole spectrum ranging from ultraviolet (UV) to far infrared (IR). The bandgaps can also be tuned continuously via adjusting the ternary or quaternary compounds, which makes it feasible to construct optoelectronic devices in different wavelengths. With state-of-the-art synthesis methods for fabricating high-quality single-crystalline group II–VI semiconductor nanowires, strong band-edge emission (i.e., photoluminescence (PL)) has been observed due to their direct bandgap nature. Many of those compound semiconductors have a large exciton binding energy close or larger than the thermal energy of room temperature in that way. As such, excitonic effect has to be considered even at room temperature. In addition, excitons strongly couple to the radiation field.

In this chapter, we begin by introducing their various synthesis methods and growth mechanism therein. In particular, vapor phase–based synthesis methods and the most recent van der Waals epitaxy will be introduced here. Heterostructures and alloys for bandgap engineering will also be introduced. Subsequently we will focus on the steady-state study of PL from excitons, followed by the time-resolved investigation of exciton dynamics. Next, various waveguides and resonator structures based on II–VI semiconductor nanowires, and, finally, different types of nanowire lasers will be discussed.

2.2 II–VI semiconductor nanowires synthesis

The production of material is the very first important step in material research. Research in II–VI semiconductor nanowires is no different; it is of utmost relevance to allocate a serious effort in producing semiconductor nanowires with high quality to enable further studies of properties and exploration in applications (Jie et al., 2010; Utama et al., 2012b). On the other hand, it is also essential to consider the scalability and stability of the nanowire production output, which allows cost-efficient production with better performance than the existing semiconductor technology (Yang, Yan, & Fardy, 2010).

Bottom-up paradigm through synthesis and crystallization processes satisfies both the sample quality and throughput issues concurrently. Bottom-up synthesis at the nanometer scale allows production of materials with greater control of composition, structure, size, function, as well as very high-crystalline quality and low density of defects, which are comparatively harder to achieve in bulk material (Lu & Lieber, 2006). For example, it has been routinely reported to have II–VI nanowires from synthesis having PL with only weak defect features (Huang et al., 2001c). On the other hand, a single-step synthesis has been demonstrated to obtain large-scale nanowire products on a wafer scale (Greene et al., 2003).

Here, we would like to discuss the synthesis approaches, particularly with precursors from vapor phases, that are used for the synthesis of II–VI semiconductor nanowires. Recent developments on synthesis, such as van der Waals epitaxy, will be discussed. Topics of particular importance such as heterostructures and bandgap engineering are also highlighted.

2.2.1 Growth mechanism and methodologies

The most commonly used approach to synthesize nanowires from vapor phase is due to the vapor–liquid–solid (VLS) mechanism (see Figure 2.1(a)), which is described as follows (Wagner & Ellis, 1964; Wu & Yang, 2001). The synthesis is initiated by generating the vapor phase of the precursor material and transporting the vapor to a substrate. For VLS growth to occur, the substrate contains metal particles, which can be liquefied at high temperatures. Such metal particles can be made by annealing a predeposited film; however, directly dispersing particles with narrow statistical distribution of diameter will have the benefit of controlling the diameter of the ensuing nanowires (Cui, Lauhon, Gudiksen, Wang, & Lieber, 2001). Au film or particle catalyst has been most commonly used due to its widespread availability, safety, and chemical stability, although other metal catalysts have also been considered (Schmidt, Wittemann, Senz, & Gösele, 2009). Ideally, the particle needs to be inert to the precursor material. The particles act as preferential adsorption sites of the vapor due to the high sticking coefficient in liquid phase. The adsorbed vapors create a liquid alloy with the metal. With continual incorporation of the vapor, the particles undergo supersaturation, which drives a nucleation at a specific part of the particle. Crystallization of the solidified matter continues from the single nucleation part, creating a one-dimensional growth as nanowire. The presence of a metallic particle

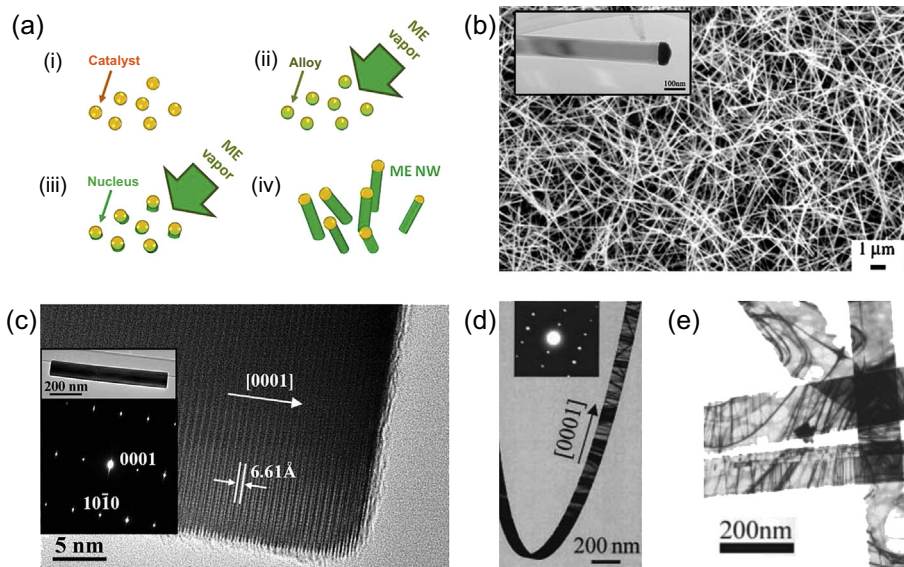


Figure 2.1 (a) The four stages in VLS mechanism of nanowire growth: catalyst, alloying, nucleation, and crystallization in 1D ME nanowires ($M = \text{Cd}, \text{Zn}$; $E = \text{S}, \text{Se}, \text{Te}$). (b) Scanning electron microscopy (SEM) image of Au-catalyzed ZnO nanowire by VLS mechanism. Inset: transmission electron microscopy (TEM) image near the tip of nanowire. Au particles can be seen as the dark contrast at the tip. (c) High resolution TEM image of CdSe nanowires. Inset: low magnification TEM and electron diffraction pattern, indicating that the nanowire grows in c -axis. TEM images of (d) ZnO and (e) ZnS nanobelts grown by VS mechanism. Inset: electron diffraction pattern.

Figure 2.1(b) adapted from Huang et al. (2001c). Figure 2.1(b) inset adapted from Yang et al. (2002). Figure 2.1(c) adapted from Utama et al. (2011). Figure 2.1(d) adapted from Pan, Dai, and Wang (2001). Figure 2.1(e) adapted from Jiang et al. (2003) with permission.

at the tip of nanowires is generally taken to be an indication of a VLS growth (Figure 2.1(b) inset).

VLS has been demonstrated for all II–VI semiconductor compounds. While VLS is widely successful, there is one major concern: the metal catalyst may diffuse into the nanowire as a contaminant (Hannon, Kodambaka, Ross, & Tromp, 2006; Allen et al., 2008). Such contaminant may act as a recombination center of charge carriers, which limits the performance of the device applications of the sample. Thus, other growth mechanisms of nanowires have also been considered. For example, there is also a special case of VLS in which no intentional introduction of foreign catalytic species is done on the substrate, where the catalytic particles come from the metallic constituent (Zhu & Bando, 2003). Such self-catalytic growth mechanism is also attractive as it reduces the possibility of contamination into the nanowire structure as the catalyst may also be consumed to become part of the structure. In vapor–solid (VS) mechanism, no metallic catalyst is needed since the vapor phase undergoes spontaneous condensation into solid phase. It is also possible for both VLS growth to occur in

giving 1D elongation while VS mechanism coexists to provide lateral encroachment in a “nanobelt” structure (Pan et al., 2001; Jiang et al., 2003).

With regard to the methodologies, II–VI nanowire synthesis utilizing precursor from vapor phase is holding traction in the research community and has also been reported for all II–VI compounds (i.e., ZnO (Huang et al., 2001c; Kong, Yu, Zhang, Fang, & Feng, 2001; Utama et al., 2012a), ZnS (Jiang et al., 2003; Wang, Zhang, Liang, Wang, & Peng, 2002b; Xiong, Wang, Reese, Voon, & Eklund, 2004b), ZnSe (Xiang et al., 2003; Zhu & Bando, 2003), ZnTe (Huo et al., 2006; Utama et al., 2013a, 2013b), CdS (Utama et al., 2011; Wang, Meng, Zhang, Liang, & Zhang, 2002a), CdSe (Ma, Moore, Ding, Li, & Wang, 2004), and CdTe (Neretina et al., 2007)). Vapor phase synthesis is also a prerequisite for achieving the aforementioned VLS mechanism. High temperature synthesis with vapor phase allows controlled crystallization of the nanowire with fewer defects. A simple case of vapor phase synthesis is by vapor transport and deposition, commonly referred to as chemical vapor deposition (CVD). The method is done by evaporating solid sources (generally in the form of powder or pellets), which are carried away by a determined gas flow (Dai, Pan, & Wang, 2003). The vapor could react in the gas phase and then deposit onto the substrate and crystallize to form the nanowire. There are also variants of such vapor phase synthesis from solid sources, such as those that uses pulsed laser to sputter the material and vaporize it. This method is referred to as “laser ablation” synthesis and was among the earlier methods used to produce semiconductor nanowires (Morales & Lieber, 1998). Laser ablation has found applications for the synthesis of II–VI nanowires (Duan & Lieber, 2000) although it is arguably not as popular as the CVD method.

Other than with powder precursor, some synthesis can also be conducted with metalorganic precursor liquids that can be introduced into vapor with a bubbler mechanism. The precursors undergo pyrolytic decomposition atop the substrate and then react accordingly to form the intended chemical compounds on the substrate. This method is called metalorganic CVD (i.e., MOCVD) and is also very successful in producing high quality II–VI nanowires in large-scale areas (Zhang, Liu, Leung, Li, & Hark, 2003). A more advanced technique is molecular beam epitaxy (MBE), which introduces the precursor to the substrate in a slow and controlled manner (Cho & Arthur, 1975). MBE utilizes Knudsen cell and ultra-high vacuum in the reaction chamber, so as to produce II–VI nanowire samples with high purity and crystalline quality (Chan et al., 2003; Chan et al., 2008; Heo et al., 2005; Janik et al., 2006). However, the production rate of sample in MBE is generally slower compared to other synthesis methods, and the utilization of MBE for II–VI nanowires growth is not as prevalent as for the III–V nanowire family.

2.2.2 Nanowire array with heteroepitaxy and van der Waals epitaxy

If there is epitaxy during the nanowire growth, that is there exists a crystalline orientational relationship between that of the substrate and that of the nanowire, the nanowires may grow into specific orientations atop the substrate. An especially interesting case is when the fast growth plane of the nanowire (for II–VI nanowires, it is generally

$\langle 111 \rangle$ for cubic phase and $\langle 0001 \rangle$ for hexagonal phase) is parallel to the surface of the substrate, which will result in arrays of vertically oriented nanowires. The strong advantage of heteroepitaxy is the possibility to control the nucleation position to form ordered arrays. Lithography can be performed on these epitaxial nanowires for integration in device applications (Fan, Werner, & Zacharias, 2006; Hochbaum, Fan, He, & Yang, 2005).

In a conventional epitaxial growth, the atoms of the nanowire and the substrate at the interface will form chemical bonds. Thus, an epitaxy typically requires a similarity on the lattice constant and the crystalline symmetry between the interfacing planes of nanowire and the substrate to avoid undue strain or even formation of crystalline defects at the heterointerface (Matthews & Blakeslee, 1974). The lattice matching and symmetry requirements are a nonissue for homoepitaxy, epitaxy where the nanowire and substrate are of the same material and phase, such as demonstrated in ZnS nanowires on ZnS crystal (Jiang et al., 2006) or ZnO nanowires on ZnO coating (Peterson, Fields, & Gregg, 2004). However, this is an issue that needs to be taken care of for heteroepitaxial nanowire array, which encompasses various systems that are of research interest. It is indeed true that the small diameter of the nanowires made the lattice matching requirement less stringent (Ertekin, Greaney, Chrzan, & Sands, 2005; Glas, 2006), and theoretical calculations and experiments show that lattice matching in heteroepitaxial nanowire array is still a relevant issue (Shi & Wang, 2010; Tomioka, Motohisa, Hara, & Fukui, 2008). While certain II–VI compounds have a fairly established choice of substrate for heteroepitaxy, e.g., ZnO on sapphire (Huang et al., 2001b), the existing lattice mismatch — however miniscule — contributes to a larger effect of strain on the system at larger nanowire dimensions, ultimately forcing defect nucleation as the more energetically favorable pathway to partially relax the strain.

When the substrate contains no active dangling bonds (e.g., materials with layered crystal such as muscovite mica, transition metal dichalcogenides) the heterointerface in the epitaxy is only bound by van der Waals interaction (Koma, Sunouchi, & Miyajima, 1984). This situation is called van der Waals epitaxy. Since van der Waals interaction is much weaker than a typical chemical bond, the lattice of epitaxial crystal is not strained immensely even when large lattice mismatch exists. In fact, nearly complete lattice relaxation can occur even in the first monolayer of epitaxial material (see schematic in Figure 2.2). Thus, nanowire arrays from many compounds can practically be grown on substrate with no dangling bonds by the van der Waals epitaxy (for II–VI nanowires, see Figure 2.2) (Utama et al., 2013c). Van der Waals epitaxy on nanowire array was first reported on cadmium chalcogenides (CdS, CdSe, CdTe) grown on muscovite mica by CVD method (Utama et al., 2011). Characterizations of the interface of ZnO nanowire on muscovite by means of electron microscopy show that van der Waals epitaxy allows lattice relaxation without defect nucleation from the first few monolayers, although a remarkably large lattice mismatch exists in the system (Utama et al., 2012a). Notably, the van der Waals epitaxy has also been shown to be applicable not just to II–VI nanowire array from vapor phase but also to other nonplanar II–VI nanostructures (e.g., tripods (Utama et al., 2012c), tetrapods (Utama et al., 2013a)), nanowire synthesized from solution phase at

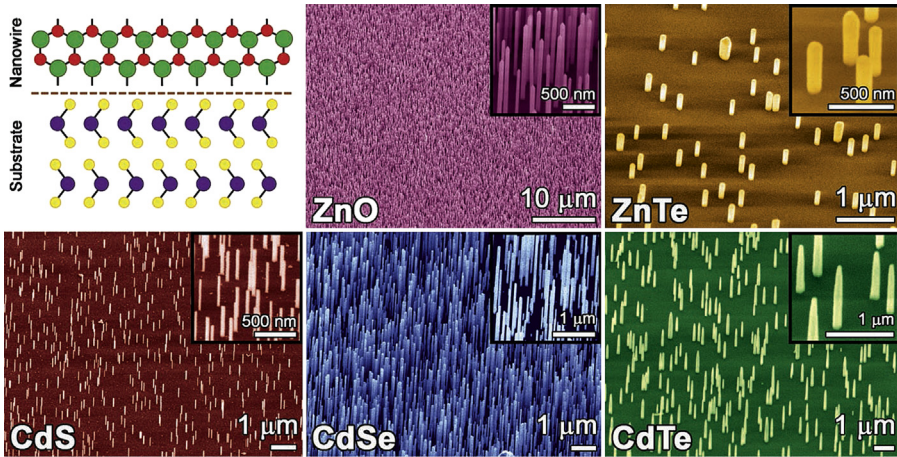


Figure 2.2 Schematic illustration of van der Waals epitaxy on a lattice-mismatched system of a nanowire on a layered substrate. SEM images of vertically aligned II–VI nanowires on muscovite mica are shown. All SEM images are pseudocolored and collected in 45° tilted view. SEM images are adapted from Utama et al. (2013c) with permission.

temperatures below 100 °C (Zhu et al., 2013), and other nanowire-substrate systems, especially III–V semiconductors on graphene (Hong & Fukui, 2011; Hong, Lee, Wu, Ruoff, & Fukui, 2012; Mohseni et al., 2013; Munshi et al., 2012).

2.2.3 Heterostructures and alloy for bandgap engineering

It is also possible to combine multiple II–VI compounds within a single nanowire structure. In the case where the constituent compounds are not mixed and each remains in binary form, it becomes a nanowire heterostructure (Lauhon, Gudiksen, & Lieber, 2004). Heterostructure is generally achieved by performing multistep synthesis, where the precursor for each constituent is introduced separately in a different step. The constituent will then be connected epitaxially to the constituent synthesized in the preceding steps. The epitaxy is enabled by the fact that the lattice relaxation in nanoscale diameter is accommodated effectively. Additionally, the lattice constants of II–VI semiconductors are not too different from each other; excluding ZnO, the lattice constants range from 5.4 Å in ZnS to 6.5 Å in CdTe (both in the <01–10> of hexagonal phase) (Adachi, 2005). On the other hand, other investigators have also reported that one-step synthesis is also possible, such as the MOCVD growth of CdS/ZnS core–shell nanowires (Hsu & Lu, 2004), due to the difference in the reactivity of each precursor.

Nanowire heterostructures can be divided into axial heterostructures and core–shell (radial) heterostructures, according to how the two or more constituents are arranged within the nanowire (see Figure 2.3(a)). For II–VI nanowires, both forms of heterostructures are of great interest for electronics and optoelectronic applications. For example, ZnO/ZnS axial nanowires were used to harvest mechanical energy into

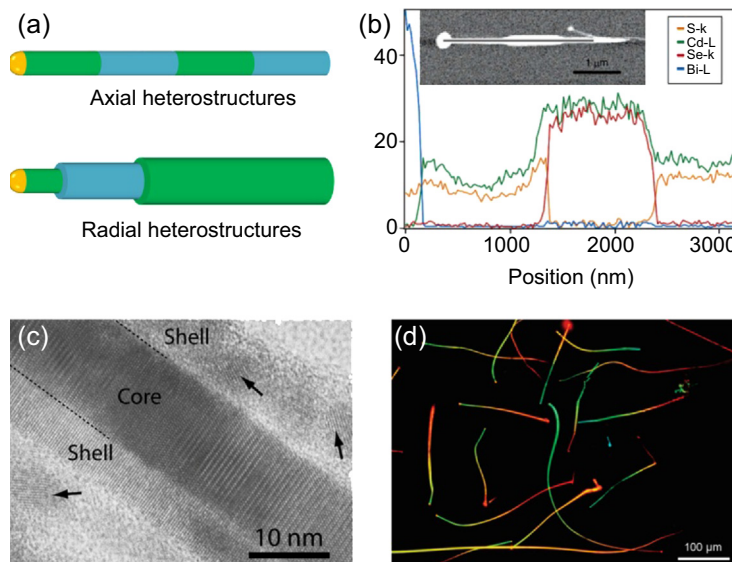


Figure 2.3 (a) Schematic illustration of axial and radial (core–shell) nanowire heterostructures from two different materials. (b) Composition line scan of a bi-catalyzed CdS/CdSe/CdS axial nanowire heterostructure along the direction shown with a black line in the SEM image at the inset. (c) A high resolution TEM image of a core–shell CdSe/ZnTe nanowire. (d) Real color photograph of CdSSe nanowires on MgF₂ substrate under 405 nm laser illumination.

Figure 2.3(b) adapted from Ouyang, Maher, Yu, McCarty, and Park (2006). Figure 2.3(c) adapted from Goebel et al. (2008). Figure 2.3(d) adapted from Gu et al. (2011) with permission.

electricity (Lu et al., 2009). Axial heterostructure with controllable periodic modulation can create nanowire superlattice, as demonstrated for ZnS/CdSe nanowires grown by atomic layer deposition (Solanki, Huo, Freeouf, & Miner, 2002) or CdS/CdSe from solution-liquid-solution synthesis (Figure 2.3(b)) (Ouyang et al., 2006).

Core–shell nanowires are very attractive for solar cells as it orthogonalizes the photon absorption and charge carrier collection directions such that each process can be efficient. Both the junction area and the minority charge carrier collection lengths are also reduced in core–shell nanowire in contrast to its film counterpart (Fan et al., 2009). As II–VI semiconductors have bandgap that is within the visible range, II–VI nanowire heterostructures have been considered as the building block for solar cell devices, such as ZnO/CdS (Tak, Hong, Lee, & Yong, 2009), ZnO/ZnS (Wang et al., 2010a), ZnO/ZnSe (Wang et al., 2008), and ZnO/ZnTe (Chao et al., 2010; Schrier, Demchenko, Wang, & Alivisatos, 2007). Other optoelectronic applications are also reported, such as their use in photoelectrochemistry (Wang et al., 2010b). In addition, the presence of shell on the nanowire may passivate surface states and further confine the charge carrier when the shell bandgap is larger than the core material (type I heterojunction, such as CdS/ZnS nanowire (Datta, Panda, & Chaudhuri, 2007)), improving the PL quantum efficiency, similar to the case of core–shell quantum dots (Dabbousi et al., 1997).

Aside from the synthesis of pristine II–VI materials, it is of interest to produce alloyed nanowires with combination of two different compounds. Some II–VI compounds (e.g., CdS and CdSe, CdSe and ZnSe) have good solubility to each other such that alloying can be performed without disintegration of the constituent compounds. As a result, such compounds can be made into a single alloy nanowire with uniform chemical composition without phase segregation. By carefully controlling the flux ratio of precursors during the synthesis, it is even possible to synthesize a graded composition nanowire, where the stoichiometry of the alloyed wire changes from one end to the other end (see Figure 2.3(d)) (Gu et al., 2011).

In II–VI nanowires, quaternary alloy (e.g., $\text{Zn}_x\text{Cd}_{1-x}\text{S}_y\text{Se}_{1-y}$, with $0 < x, y < 1$) (Pan, Liu, Sun, & Ning, 2010) and ternary alloy (e.g., $\text{CdS}_x\text{Se}_{1-x}$ (Pan et al., 2005b) and $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ (Venugopal, Lin, & Chen, 2006)) have both been reported. Generally, the crystal lattice parameters of the alloy are scaled proportional to the concentration of the constituent compounds, a rule commonly known as Vegard's law. A more useful characteristic of a semiconducting alloy is that the bandgap of the alloy is a function of the constituent concentration, thus allowing to tune the emission wavelength of the nanowire. For example, the emission of ZnCdSSe nanowire could range from 350 nm (pure ZnS) to 710 nm (pure CdSe), covering the visible range of emission (Pan et al., 2010). Due to the change of lattice parameters with composition, it is also useful to exploit van der Waals epitaxy in achieving alloyed nanowire array over the whole compositional span, as a conventional heteroepitaxy would have dictated that the substrate be able to accommodate a range of lattice mismatch value (Pan et al., 2012).

2.3 Steady-state photoluminescence spectroscopy

Owning to their direct bandgap nature ranging from UV to NIR, the PL properties of II–VI semiconductor nanowires have been intensively studied over the past decades, which is crucial for constructing integrable optoelectronic devices (Utama et al., 2012b). Benefiting from their large surface-to-volume ratios, high-crystalline qualities, and dimensions that are comparable to the characteristic length of excitons therein, distinct properties of II–VI semiconductor nanowires are discovered with respect to the bulk, such as the size and surface effects that remarkably influenced their optoelectronic properties (Jie et al., 2010). Especially, exciton dynamics and related interesting phenomena probed by steady-state PL will be discussed in detail here.

2.3.1 Exciton: free exciton, bound exciton, and the others

As is well known, excitons are one kind of bosonic quasiparticle consisting of bound electron–hole pairs through Coulombic force. Besides free excitons generated by external excitations, bound exciton, that is an electron–hole pair bound to a point defect (such as ionized donor, neutral donor, or neutral acceptor), offers additional Coulomb energy to make the bound exciton energy lower than that of the free neutral

exciton, resulting in redshifted PL peak and broadened peak width. Similarly, the free excitons can bind to each other to form a new quasiparticle, such as biexcitons. Excitons show superior characteristics compared to free charge carriers, such as large oscillator strength, strong coupling with phonons. In II–VI semiconductor nanowires, excitons couple strongly to the radiation field, giving rise to intense PL signals. At low temperatures, a large part of exciton emission comes from phonon replica and bound excitons, donor–acceptor pairs, or other defect centers, which is important for getting complete knowledge of PL properties. For one-dimensional II–VI semiconductor nanowires, we will focus on the Wannier-type excitons only.

Typically, excited electrons will return to the ground state by several recombination processes as summarized in Figure 2.4(a). The possibilities of different recombination processes are strongly dependent on the samples (e.g., defect levels) and experimental conditions (e.g., temperature and excitation energy). The defects inside the crystalline structure can trap electrons, holes, and excitons, which form bound exciton complexes.

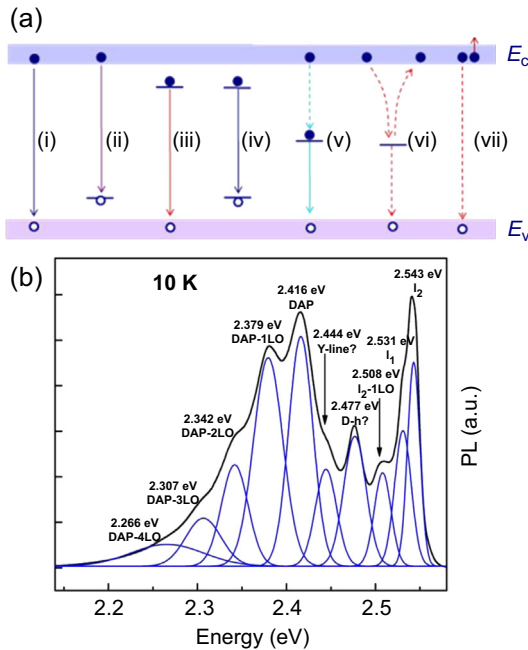


Figure 2.4 (a) Categories of recombination process inside semiconductors: (i) band-to-band recombination; (ii) band-to-acceptor recombination; (iii) donor-to-valence recombination; (iv) donor-to-acceptor pair recombination; (v) recombination via a deep center in the bandgap; (vi) nonradiative recombination via an intermediate state; (vii) band-to-band Auger recombination. (b) PL fine structure of CdS nanobelts measured at 10 K with a 325-nm He–Cd laser excitation.

Figure 2.4(a) adapted from Utama et al. (2012b). Figure 2.4(b) adapted from Xu et al. (2011) with permission.

Fundamental physics thus becomes very complicated and requires comprehensive investigations since these bound exciton complexes will interact with each other as a function of temperature or excitation energy.

Experimentally, for example, [Xu et al. \(2011\)](#) measured the PL spectrum from CdS nanobelts at 10 K with a 325 nm laser excitation as shown in [Figure 2.4\(b\)](#). The distinct peak positions were determined and assigned to different categories of recombination. Due to the crystal field and spin-orbit coupling, the valence band of wurtzite CdS was split into three with respective energies of $E_A = 2.550$ eV, $E_B = 2.568$ eV, and $E_C = 2.629$ eV. The emission peak located at 2.543 eV was ascribed to neutral donor bound excitons (D^0X), usually labelled as I_2 . Another peak near 2.531 eV, usually labelled as I_1 , was attributed to neutral acceptor bound excitons (A^0X). The peak at 2.508 eV was identified as the longitudinal (LO) phonon (around 38 meV) replicas of I_2 , accompanied by the emission of one LO (i.e., D^0X -LO). The origin of peak at 2.477 eV was possibly attributed to holes bound to the donors, while the 2.444 eV peak was attributed to the Y-line due to a weak LO coupling. The peak at 2.416 eV was identified as DAP emission, which can be widely found in other wideband II–VI semiconductors. In addition, the following peaks at 2.379, 2.342, 2.307, and 2.266 eV were assigned as multiple phonon replicas with one LO-phonon energy spacing (~ 38 meV). Note that the exciton–phonon coupling for DAP was stronger than for excitons bound to impurities (I_2), from the calculated Huang-Rhys factor S ([Zhao & Kalt, 2003](#)), which was consistent with the statements of [Moroz, Brada, and Honig \(1983\)](#). Furthermore, the first principle calculation verified the chemical nature of the intrinsic donors and acceptors in CdS ([Xu et al., 2011](#)). It was concluded that the dominant contribution of the shallow donors was due to the sulfur vacancies

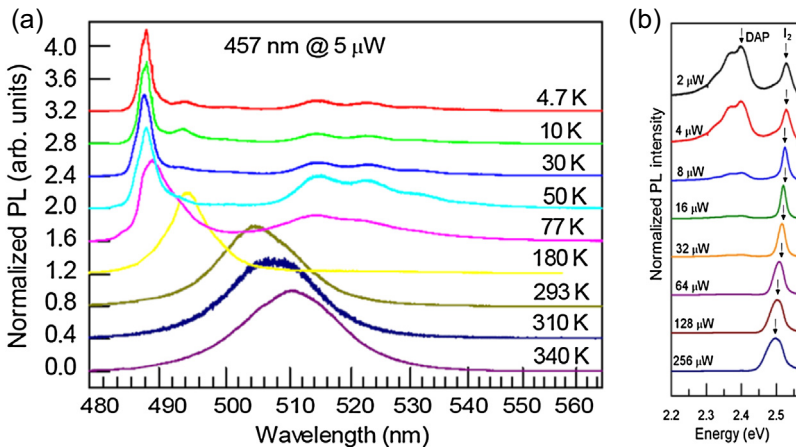


Figure 2.5 (a) Temperature-dependent PL spectra of the ZnTe nanobelts in the range from 13 to 240 K with 473 nm excitation laser of 57 μ W. (b) Evolution of the PL spectra of CdS nanowires measured at 10 K with 470 nm laser excitation under different excitation densities.

[Figure 2.5\(a\)](#) adapted from [Zhang et al. \(2012a\)](#). [Figure 2.5\(b\)](#) adapted from [Xu et al. \(2011\)](#) with permission.

with E_D around 100 meV and the acceptors originated from the cadmium vacancies with E_A around 160 meV, in good agreement with experimental results shown in Figure 2.4(b).

2.3.2 Temperature-dependent photoluminescence

By performing the temperature-dependent spectroscopy measurements, different categories of recombination, such as recombination dynamics of FX, excitons bound to neutral impurities (D^0X or A^0X), and DAP can be further systematically identified. For example, Zhang et al. (2012a) carefully analyzed the temperature-dependent PL spectrum evolution of ZnTe nanobelts with high spectral resolution spectroscopy and gave a clear picture about exciton behavior from 13 to 240 K, as shown in Figure 2.5(a). Generally, the total intensity of PL emission decreased with increasing temperature. The peak splitting of PL emission can be clearly seen while the temperature increased to 90 K and the new peak (i.e., 2.30 eV) can be assigned to DAP emission. In addition, the temperature-dependent red shift of PL peak could be readily observed with increasing temperature, which is attributed to increased electron–phonon interaction and the lattice expansion with increasing temperature (Varshni, 1967). This temperature-dependent PL peak evolution can be qualitatively described by the Varshni equation (O’donnell & Chen, 1991). The FX emission became stronger with the temperature increasing to room temperature. This is because the PL emission of bound excitons would be thermally ionized and FX emission becomes dominant with increasing temperature. Moreover, thermal broadening of PL peak widths was experimentally observed while increasing the temperatures, which was ascribed to the strong interaction between excitons and acoustic/longitudinal phonons (Chen et al., 2010; Zhang et al., 2012a).

2.3.3 Power-dependent photoluminescence

The power-dependent behavior of PL in II–VI semiconductor nanowires is another important property to be investigated. Figure 2.5(b) depicted a typical PL spectra measured under different excitation densities (Xu et al., 2011). One can easily observe two peaks from the spectra measured, which were denoted as bound exciton (I_2) and DAP, respectively. It was interesting to see that while increasing the excitation power, DAP quickly saturated compared with I_2 and could not be resolved as the excitation increased to 5 μ W pump power. The saturation here suggested that DAP emission due to the cadmium vacancy would easily be fully populated as the pump power increased. The peak positions of I_2 underwent gradual red shift with increased excitation energies, possibly due to the laser heating effects (Yang et al., 2005).

2.3.4 Exciton–phonon interaction

It is also interesting to investigate the strong exciton–phonon interaction inside the II–VI semiconductor nanowires. As the size goes to nanoscale, the coupling between excitonic and vibrational states will be very different from that of their bulk

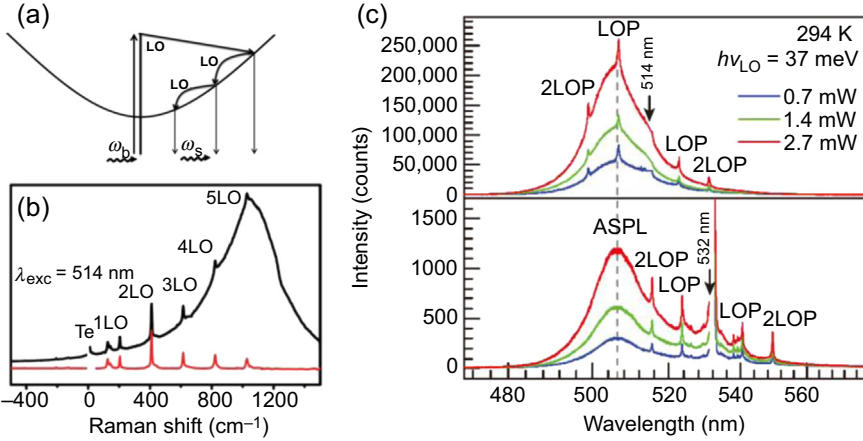


Figure 2.6 (a) Schematics of acoustic and longitudinal optical phonon scattering processes under resonant condition (i.e., general multi-LO-phonon scattering process). (b) A typical resonant Raman spectra of a single ZnTe nanorod with 514 nm excitation at room temperature. The black and red/dark gray curves show the original and PL subtracted spectra, respectively. (c) Room temperature anti-Stokes PL spectra of a single CdS nanobelt with 514-nm (top) and 532-nm (bottom) laser excitations at three power levels.

Figure 2.6(a) and (b) adapted from Zhang et al. (2012b). Figure 2.6(c) adapted from Zhang et al. (2013) with permission.

counterparts. In general, when a photon with energy larger than the bandgap excites the semiconductor, an exciton will be induced; then one LO-phonon is generated and the corresponding exciton is scattered to an actual parabolic dispersive excitonic state; next, the scattered exciton recombines with one scattered phonon emitted or scattered by another LO-phonon. This described cascaded scattering process (as shown in Figure 2.6(a)) continued until the momentum of exciton reached a $q = 0$ point (Zhang et al., 2012b). Resonant Raman scattering (RRS) is an effective technique to probe such strong exciton–phonon interaction (Wang, Xu, & Jin, 2004; Permogorov, 1975). The cross-section of LO-phonon scattering can be significantly enhanced in the resonant condition, indicating the dominant Fröhlich electron–phonon interaction mechanism. Zhang et al. (2012b) performed RRS investigation of cubic ZnTe nanorods near the direct bandgap. As shown in Figure 2.6(b), up to fifth-order LO fingerprint can be resolved by using a 0.17 mW excitation of 514 nm. The Huang-Rhys factor (known as figure of merit of the electron–phonon interaction strength) was evaluated, which was considerably large and increased from 3.2 to 4.8 as the nanorod diameter increased from 90 to 200 nm.

As well, strong anti-Stokes PL have been experimentally seen in II–VI semiconductor nanowires such as CdS nanobelts, which benefitted from strong exciton–phonon interactions (Li, Zhang, & Xiong, 2013a; Zhang, Li, Chen, & Xiong, 2013). As shown in Figure 2.6(c), by using a 532-nm laser (bottom) and a 514-nm laser (top) excitations at room temperature under three different pump powers, strong anti-Stokes PL emission with its peak of 506 nm can be clearly identified, which was facilitated by resonant

annihilation of multiple LO. For CdS nanobelts, the much smaller surface recombination velocity (Huppert, Evenor, & Shapira, 1984) and much lower Auger nonradiative recombination (Imangholi, 2006) facilitated the near-unity external quantum efficiency ($>99\%$), which is one of the stringent requirements toward laser cooling of semiconductor, theoretically discussed by Sheik-Bahae and Epstein (SBE) (Sheik-Bahae & Epstein, 2004, 2009). Zhang et al. (2013) thus, for the first time, demonstrated a net cooling by about 40 K in semiconductors. Their findings suggested that II–VI semiconductor with strong exciton–phonon interactions could be harnessed to realize laser cooling and pave the way for optical refrigeration based on semiconductors.

2.4 Time-resolved photoluminescence spectroscopy

2.4.1 Introduction: setup and decay channels

As introduced above, steady-state PL spectra are widely used to study the origin and type of excitons in semiconductors and further give us a picture of near bandgap electronic structure. However, to further explore the dynamics of exciton from generation, transport, to recombination etc., ultrafast spectroscopy techniques are needed. The exciton behaviors in timescale are especially important in the optimization of the semiconductor nanostructure devices. Typically, three steps are involved in a PL process in direct-bandgap semiconductor (Sundaram & Mazur, 2002): (1) after absorbing a photon, an electron in valence band jumps into conduction band, which leaves a hole in valence band (optical excitation); (2) the electron releases its excess energy via electron–phonon scattering or electron–electron scattering (thermalization); (3) exciton recombines and returns to equilibrium states with emission of photons (radiation transition) or not (nonradiative transition). The optical excitation occurs in 0.01–1 ps. The thermalization via carrier–carrier scattering and carrier–phonon scattering has a typical timescale of ~ 0.01 –1 ps and 0.1–1 ps, respectively. The exciton recombination rate is much slower compared with the above two processes. For widely studied II–VI semiconductors such as CdS and ZnO, the radiative exciton lifetime is ~ 0.1 –10 ns (Dovrat, Goshen, Jedrzejewski, Balberg, & Sa’ar, 2004; Hong, Joo, Park, Jun, & Yi, 2003; Leigh, Howard, Jan, & Chennupati, 2010; Liu, Zhang, Xing, Xiong, & Sum, 2013a; Liu, Zhang, Xiong, & Sum, 2013b). The lifetime of nonradiative transition associated with defect states is shorter than the radiative transition. In the following paragraphs, we will discuss the recombination dynamics and mechanisms in II–VI semiconductor nanostructures in detail.

Two time-resolved spectroscopy methods are well established in studying exciton dynamics: transient absorption (TA) spectroscopy (Berera, Van Grondelle, & Kennis, 2009) and time-resolved photoluminescence (TRPL) spectroscopy (So, Dong, Berland, French, & Gratton, 2002). The absorbance or photoemission is probed as a function of time after the materials are pumped by a short-pulsed laser (femto-second, picosecond, and so forth). In this case, the pulse duration is a limiting factor to the time resolution. Here we focus on uncovering the exciton recombination process of semiconductor nanostructures using TRPL spectroscopy.

2.4.2 Radiative versus nonradiative recombination

For direct bandgap II–VI semiconductors, radiative recombination occurs in band-to-band transition in most cases. The inevitably formed defects or impurities result in additional electronic states inside the bandgap. The exciton recombination can be accomplished via the intermediate defect states with the releasing of photons. However, the defect states, as well as surface states, result in noticeable nonradiative transition, which hampers optical and optoelectronic performance of the semiconductor device. For example, the nonradiative transition reduces the emission intensity and quantum efficiency of luminescence, which is not good for LED, laser, optical cooling, and so forth (Guzelturk et al., 2014; Zhang, Ha, Liu, Sum, & Xiong, 2014a; Zhang et al., 2013). Besides, the nonradiative transition rate is generally faster than the radiative rate, which causes a decreased overall carrier lifetime and thus reduces the efficiency of optoelectronic devices such as solar cells. In nanostructures, big amounts of surface states exist due to the large surface-to-volume ratio (Guzelturk et al., 2014). Especially, when the nanostructure size is smaller than the exciton diffusion length, the possibility of excitons trapped by the surface states is further enhanced, which inevitably increases the probability of nonradiative transition. The surface states can be mitigated by passivating the surface considering the specific surface chemistry properties.

Both the radiative and the nonradiative recombination contribute to time-resolved properties of PL. Figure 2.7(a) shows the room-temperature TRPL spectroscopy of individual CdS nanowires (diameter: 120 nm) before and after coating of poly(methyl methacrylate) (PMMA) (Liu et al., 2013a). The excitation source was a frequency-doubled pulse (400 nm) from a titanium-sapphire oscillator (pulse width: 120 fs, repetition rate: 76 MHz), and a streak camera was used for detecting with a time resolution

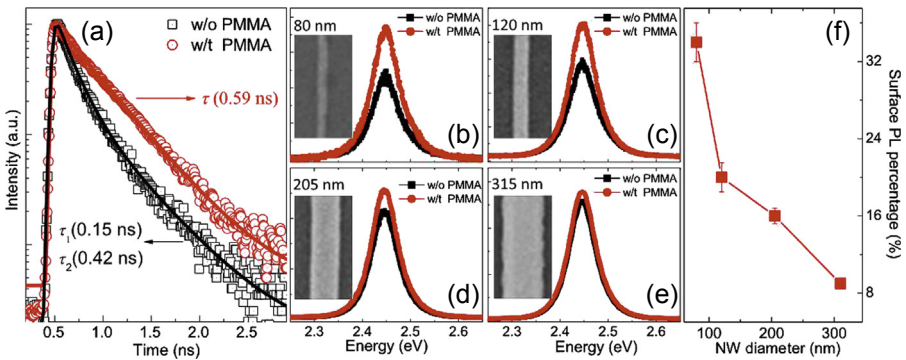


Figure 2.7 Time-resolved PL studies of CdS nanowire. (a) Time-resolved PL spectroscopy of individual CdS nanowire before and after coating of PMMA. The nanowire diameter is 120 nm. (b–e) Steady-state PL spectroscopy of CdS nanowire before and after coating of PMMA. The nanowire diameter is 80 nm (b), 120 nm (c), 205 nm (d), and 315 nm (e). (f) The surface PL percentage as a function of nanowire diameter.

Figures adapted from Liu et al. (2013a) with permission.

of ~ 6 fs. For bare CdS nanowire (without PMMA), the TRPL spectrum can be well fitted by a biexponential decay function.

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (2.1)$$

where A_1 and A_2 are weighting factors. The two time constants τ_1 and τ_2 correspond to the nonradiative and radiative transition lifetime, respectively. After coating with PMMA, the surface defects are passivated, therefore the TRPL spectrum is well fitted with a single exponential function, indicating a dominating radiative decay channel. With the suppression of surface states, the PL intensity increased (Figure 2.7(b–e)). When the nanowire diameter becomes larger, the increased percentage reduces because of the decreasing of surface-to-bulk ratio (Figure 2.7(f)).

2.4.3 Size-dependent photoluminescence lifetime

Size effect is an important issue in nanostructures. When the nanostructure size is comparable with Bohr radius, the quantum effect arises and plays a key role in excitonic properties of semiconductors (Hong et al., 2003; Moreels et al., 2009). The exciton oscillation strength decreases with the increase of quantum dots diameter (Moreels et al., 2009). Even when the size is beyond the quantum regime (~ 100 nm), the excitonic behavior is also size dependent (Liu et al., 2013a). As shown in Figure 2.8, the radiative recombination rates increased monotonically from 0.3 to 1.2 ns when the CdS nanowire increased from 80 to 315 nm, which is much larger

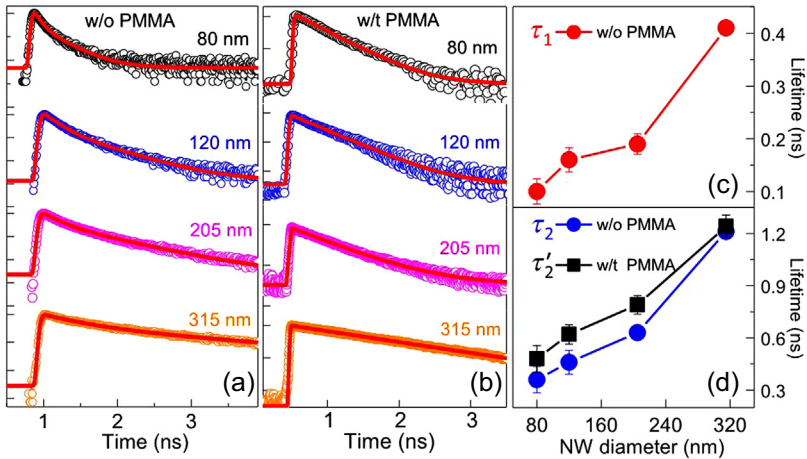


Figure 2.8 Diameter-dependent time-resolved PL spectroscopy in CdS nanowires. (a, b) Time-resolved PL spectroscopy of four CdS nanowire (diameter: 80, 120, 205, 315 nm from top to bottom) before (a) and after (b) coating of PMMA. (c, d) Nonradiative (c) and radiative (d) recombination rate as a function of nanowire diameter extracted from Figure 2.8(a) and (b). Figures adapted from Liu et al. (2013a) with permission.

than the Bohr radius of CdS (~ 2.8 nm). The size-dependence recombination rate behavior is due to the surface scattering effect. Upon the excitation, an amount of excitons diffuses to and quenches at the surface. The semiconductor diffusion length is in micrometer scale, suggesting that the exciton properties also can be affected by the structure size far beyond the quantum regime.

2.4.4 Temperature-dependent photoluminescence lifetime

The PL lifetime is also affected by temperature. Figure 2.9(a) shows the TRPL spectra of a CdS nanobelt as a function of temperature (Xu et al., 2011). Under low excitation power (left panel), the spontaneous emission lifetime increased with the decreasing of temperature as a result of suppression of surface states. The surface states population obeyed Boltzmann distribution, and the surface state related nonradiative rate can be expressed as a function of temperature (Xu et al., 2011):

$$\tau_{nr}(T) = \tau_{nr}(T = 0)K/e^{-\frac{E_a}{k_B T}}, \quad (2.2)$$

where E_a is the activation energy for a nonradiative process. From the equation, the nonradiative transition lifetime decreases and thus the average PL lifetime decreases with the increasing of temperature. With a high excitation power, the local heating is strong to cover the external temperature variation, leading to a temperature-independent spontaneous emission. On the other hand, the lifetime of stimulated emission mainly due to the radiative transition is much faster than nonradiative transition; hence the lifetime of stimulated emission does not show significant change with the temperature. Different variation trends of temperature-dependent PL lifetime

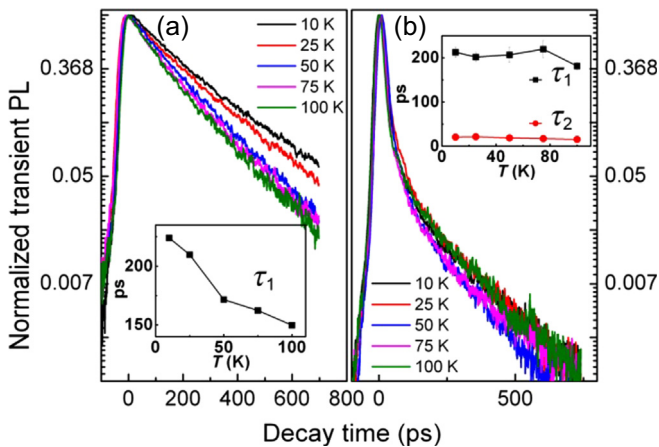


Figure 2.9 Time-resolved photoluminescence spectroscopy of CdS nanobelt as a function of temperature under low pump intensity (a) and high pump intensity (b).

Figures adapted from Xu et al. (2011) with permission.

were also observed in other semiconductors such as ZnO, which was explained by the decreased coherent extension of excitons with the increasing temperature due to the phonon scattering (Zhang et al., 2007).

2.4.5 Exciton recombination at high-power excitation

Under strong pumping conditions, the exciton population can be very high, giving rise to the multiexciton interaction processes, such as stimulated emission, Auger recombination, and biexciton recombination. The processes decrease emission lifetime but compete with each other. As Figure 2.10 shows, as the pumping intensity is higher than 28.0 J/cm^2 , exciton population inversion reaches, leading to amplified spontaneous emission (ASE) and further lasing processes (Zhang et al., 2012a). The lifetime of ZnTe nanobelt is sharply decreased at the lasing threshold (28.0 J/cm^2). Auger recombination involves three particles: an electron, a hole, and another electron or hole (Huldt, 1971). The exciton recombination energy is nonradiatively transferred to the electron or hole. In GaAs, the quantum yield and related optical performances such as lasing suffer from the low threshold of nonradiative Auger process (Saxena et al., 2013). The biexciton is formed from two excitons via dipole–dipole interaction. As the biexciton annihilates, a free exciton is left and a photon is created. The photon energy is slightly smaller than the exciton by the biexciton binding energy (Park et al., 2011). Using a simple model, two excitons decay simultaneously in biexciton

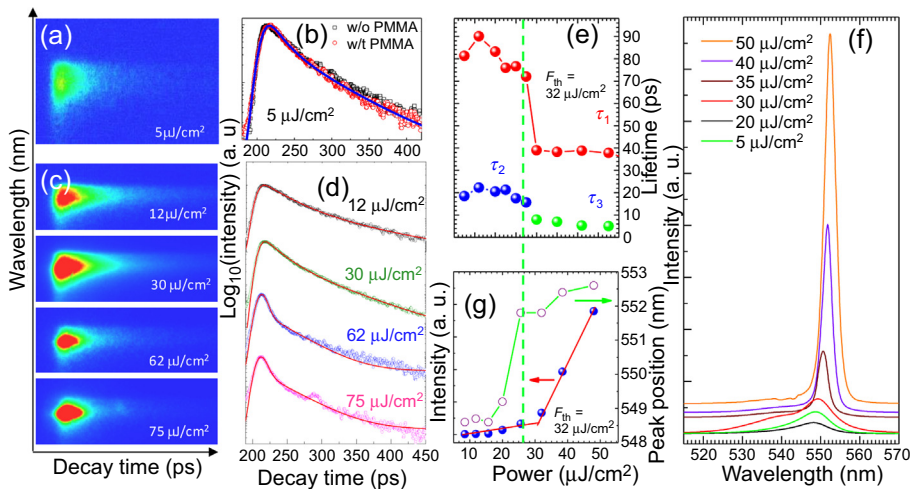


Figure 2.10 Power-dependent time-resolved photoluminescence spectroscopy of ZnTe nanobelt. The streak camera (a, c) image and time-resolved photoluminescence spectroscopy (b, d) at different pumping power (indicated around each spectrum). (e) Photoluminescence lifetime deduced from (a–c) as a function of pumping fluence. (f) Integrated output power and lasing peak line width as a function of pumping fluence. (g) Steady-state photoluminescence under different pumping influence.

Figures adapted from Zhang et al. (2012a) with permission.

recombination process, therefore, the biexciton recombination rate is doubled compared to that of a single exciton (Kono et al., 2005).

2.4.6 Surface plasmon modified exciton recombination

The spontaneous emission lifetime of semiconductors also partly depends on the environment. This means that by placing the emission center in a special environment (e.g., cavity or photonic crystal), the lifetime of spontaneous emission can be modified (Nan et al., 2014; Peng et al., 2012). The lifetime decreasing was ascribed to the Purcell effect. By controlling the distance between the CdS nanowire with Au films using a dielectric layer (e.g., SiO_2), the lifetime of the CdS emission can be tuned as shown Figure 2.11, as well as the intensity that was enhanced accordingly (see Figure 2.11(a)) (Liu, Zhang, Yip, Xiong, & Sum, 2013c). It is significant to note that the decay rate, intensity, and quantum yield enhancements (Figure 2.11(c)) can be calculated by using the Purcell theory (Purcell, 1946). Using FDTD simulation, they ascribed this lifetime decreasing to the strong electric field inside the dielectric layer, which is related to the surface plasmons in that structure. Using a whispering-gallery plasmonic nanocavity of CdS– SiO_2 –Ag core–shell nanowire devices, Cho et al. tuned the cavity size so as to match the whispering-gallery resonances, and a complete transition from thermalized exciton to hot-exciton emission was achieved, which reflected significantly high radiative rate enhancement ($>10^3$) and subpicosecond lifetimes (Cho et al., 2011). Thereafter, a nanometer-sized gap between silver nanowire and silver film was fabricated and AlQ₃ dyes were placed inside this gap. An enhancement of radiative emission rate approaching 1000 for emitters was demonstrated (Russell, Liu, Cui, & Hu, 2012).

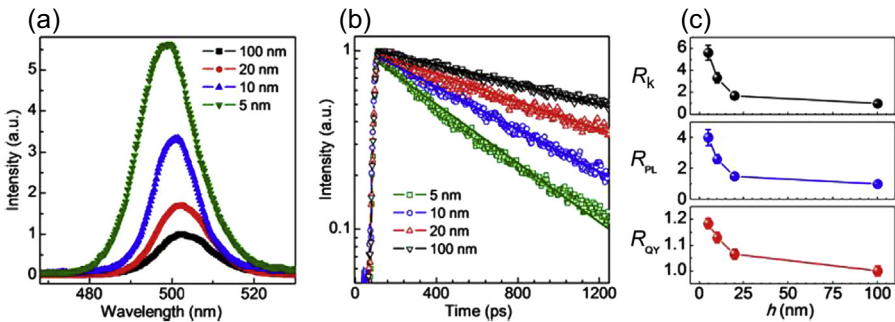


Figure 2.11 (a) Steady-state PL spectra of the four nanowires with pump power around $1.0 \mu\text{J}/\text{cm}^2$, the other three spectra are normalized using the reference sample with $h = 100 \text{ nm}$. (b) The corresponding (normalized) PL decay transients from the PL spectra as shown in panel a. (c) Thickness-dependent decay rate enhancement R_k , PL intensity enhancement R_{PL} , and the quantum yield enhancement R_{QY} factors. The $h = 100 \text{ nm}$ sample is used as the reference.

Figures adapted from Liu et al. (2013c) with permission.

2.5 Nanowire waveguides and functional devices

2.5.1 Introduction

Usually, PL generated in a nanowire can be channeled into guiding modes and wave guided along nanowire, making the nanowire an excellent active nanowaveguide for a variety of applications such as nanoscale light-emitting devices, lasers, modulators, sensors, and detectors.

Here we introduce the PL and related functional components or devices of semiconductor nanowires. Based on their excellent waveguiding properties, semiconductor nanowires have been used as building blocks for functional components and devices including optical couplers/splitters, resonators, and modulators/switchers. A brief summary is provided.

2.5.2 Waveguiding properties

At optical frequency regimes, group II–VI semiconductors usually have high refractive index and small surface roughness, making nanowires ideal waveguides for supporting tightly confined optical fields with relatively low optical losses. For a nanowire waveguide with circular cross-section, the waveguiding behaviors at transparent spectral range can be revealed by solving the following Helmholtz equations:

$$\begin{aligned} (\nabla^2 + n^2 k^2 - \beta^2) \vec{e} &= 0 \\ (\nabla^2 + n^2 k^2 - \beta^2) \vec{h} &= 0, \end{aligned} \quad (2.3)$$

where n represents the transverse refractive index profile of the waveguiding system; $k = 2\pi/\lambda$, λ represents the wavelength of the light in vacuum; and β is the propagation constant.

By numerically solving Eqn (2.3) with proper boundary conditions, several waveguiding modes supported by the nanowire can be calculated (Ma, Guo, Wu, Dai, & Tong, 2013). As shown in Figure 2.12, while diameter decreases, single-mode operation can be satisfied leaving only the HE_{11} mode (Johnson, Yan, Yang, & Saykally, 2003; Tong, Lou, & Mazur, 2004), and more fraction of guided light moves out of the nanowire as evanescent fields (Wu & Tong, 2013).

For noncircular cross-section nanowires, mode profiles can also be obtained by numerical methods (e.g., finite-element method), and corresponding guiding behavior is modified by different cross-sections of semiconductor nanowires (see Figure 2.13, for example).

2.5.3 Nanowire optical cavities

Usually, a single semiconductor nanowire with relatively high refractive index compared with environment is a natural F-P cavity as light reflects at the end faces of nanowire (Johnson et al., 2003; Yan et al., 2003b; Van Vugt, Rühle, &

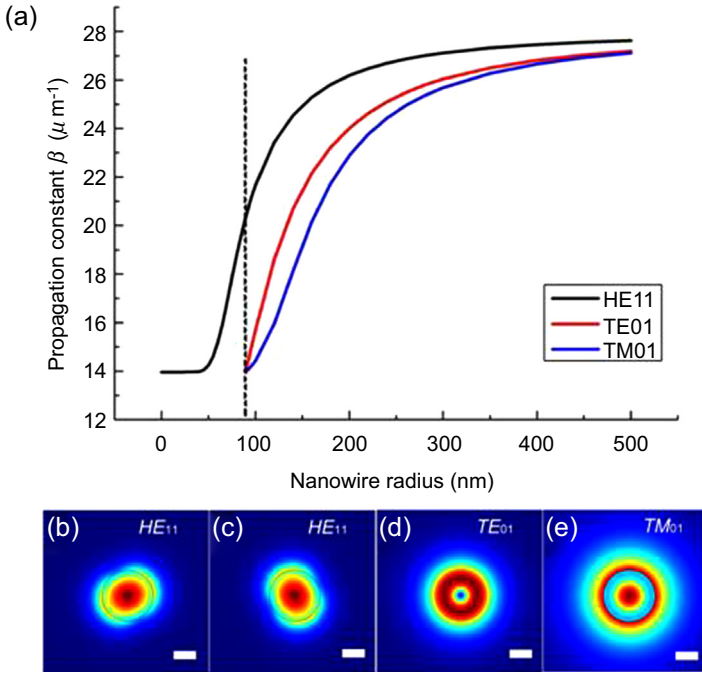


Figure 2.12 (a) Calculated propagation constants (β) of the HE₁₁, TE₀₁, TM₀₁ modes of 450-nm wavelength inside an air-clad ZnO nanowire. Single-mode condition is indicated by the dashed line. (b–d) Electric field of the HE₁₁, TE₀₁, TM₀₁ modes of 450-nm wavelength in a 240-nm-diameter ZnO nanowire. Scale bar: 100 nm. Figures adapted from [Ma et al. \(2013\)](#) with permission.

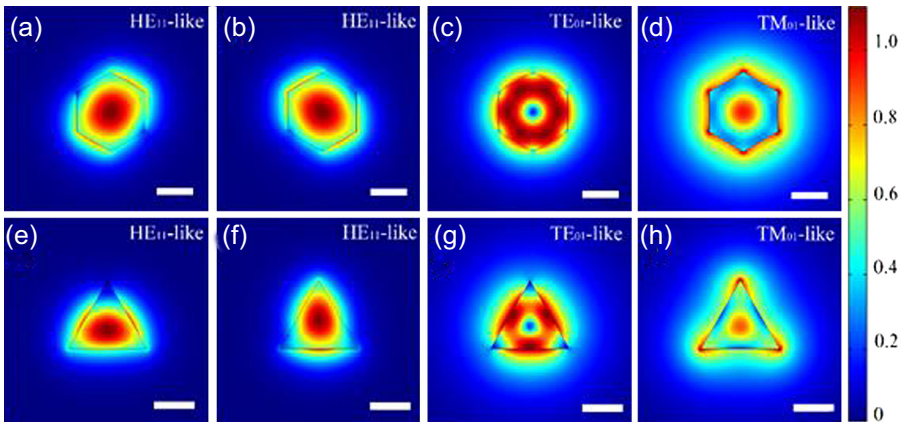


Figure 2.13 Electric field distribution of waveguided modes of a 240-nm-diameter free-standing nanowires with (a–d) hexagonal cross-section, and (e–h) triangular cross-section at 450-nm wavelength. Scale bar corresponds to 100 nm. Figures adapted from [Ma et al. \(2013\)](#) with permission.

Vanmaekelbergh, 2006; Xiao, Meng, Wu, & Tong, 2011b). However, this kind of cavity suffers from weak feedback and large substrate-induced leakage losses especially when the nanowire is very thin (e.g., diameter < 100 nm). Cavities with better performance have been demonstrated by functional nanowire structures including circular cavities (Czekalla et al., 2008, 2010; Dai et al., 2010, 2011b; Dai, Xu, Sun, & Zhang, 2011a; Dai, Xu, Zheng, Lv, & Cui, 2009; Dietrich & Grundmann, 2011; Ma et al., 2009, 2010; Nobis & Grundmann, 2005; Nobis, Kaidashev, Rahm, Lorenz, & Grundmann, 2004; Wiersig, 2003), hybrid nanowire-phonic-crystal cavities (Barrelet et al., 2006; Zhang & Loncar, 2008), and loop mirror (LM) cavities (Wang, Hu, Li, & Tong, 2009; Xiao et al., 2011a).

The single nanowire F-P cavity was formed by opposite end-face reflections from either parallel- or perpendicular-to-the-wire axis (see Figure 2.14).

Over the past years, F-P-type group II–VI semiconductor nanowire cavities have been intensively investigated. Johnson et al. (2003) studied ZnO nanowire-based waveguides and F-P cavity lasers, and demonstrated that experimental cavity features were in good agreement with theoretical analyses regarding the dielectric cylindrical waveguide cavities. Later, Yan et al. (2003b) also experimentally investigated excellent F-P microresonators based on ZnO nanoribbons. Since then, various F-P-type resonators based on group II–VI semiconductor nanowire have been intensively studied (Van Vugt et al., 2006). Xiao et al. (2011b) reported an F-P nanowire cavity composed of two coupled CdSe nanowires for single-mode lasing (see Figure 2.15).

Compared with relative low-efficient end-face reflection of the nanowire F-P cavity, circular cavity can offer much stronger feedback. Generally, there are two typical types of nanowire circular cavities, that is ring and whispering-gallery mode (WGM) cavities (see Figure 2.16).

Generally, ring cavity can be readily formed by manipulating a semiconductor nanowire into a closed loop. The light propagates along the loop and transmits through the binding site via evanescent coupling. Ma et al. (2009) reported a coupled CdS nanowire ring-F-P cavity. Hu et al. (2013) reported a free-standing CdS nanowire ring cavity with diameter less than $50\ \mu\text{m}$ (as shown in Figure 2.16(a) and (b)).

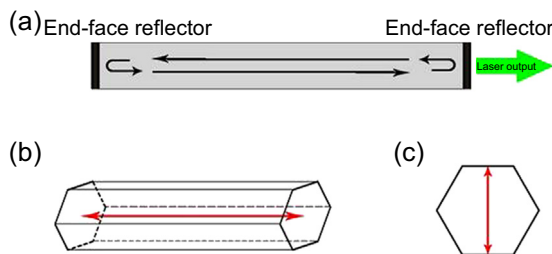


Figure 2.14 Schematics of single semiconductor nanowire F-P cavity. (a) Schematic of a single nanowire laser based on F-P cavity. (b) F-P cavity formed by end-face reflections. (c) F-P cavity formed by a hexagonal cross-section's surface perpendicular to the nanowire axis. Figures adapted from Ma et al. (2013) with permission.

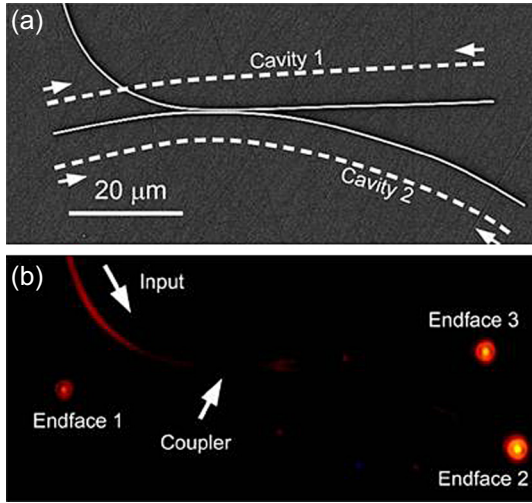


Figure 2.15 (a) Schematic of F-P cavity formed by coupled nanowires. (b) Excitation scheme of structure shown in (a).

Figures adapted from [Xiao et al. \(2011b\)](#) with permission.

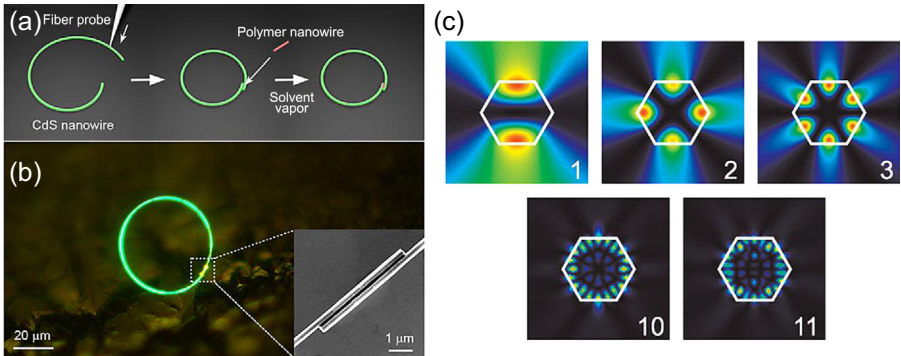


Figure 2.16 Semiconductor nanowire circle cavities. (a) Schematic of the process to splice a nanowire circle cavity. (b) The optical image of a CdS nanowire circle cavity excited by a 405-nm laser. The inset is the SEM image of the splicing area. (c) Near-field intensity patterns of a hexagonal cross-section nanowire WGM cavity. The number in the bottom right corners are mode numbers.

Figure 2.16(a) adapted from [Hu, Guo, and Tong \(2013\)](#). Figure 2.16(b) adapted from [Czekalla et al. \(2010\)](#) with permission.

For a nanowire with radius close to or bigger than the semiconductor bandgap wavelength, a WGM cavity can be easily established within the cross-section plane of the nanowire. For example, [Wiersig \(2003\)](#) reported WGM in hexagonal dielectric cavities. Besides the above-mentioned cavities, other geometries of optical cavities

have also been fabricated out of group II–VI semiconductor nanowires, such as hybrid nanowire-photonic-crystal cavities or nanowire loop mirror cavities.

Combined with the photonic crystals, nanowires could offer a distinct way to form high quality nanowire cavities (Barrelet et al., 2006; Zhang & Loncar, 2008). Barrelet et al. (2006) demonstrated a hybrid nanowire cavity by placing a CdS nanowire on a photonic-crystal microcavity structure. Zhang and Loncar (2008, 2009) further analyzed the mechanism of effectively suppressing resonator losses by designing one-dimensional photonic crystal structure at nanowire ends with theoretical calculations, as shown in Figure 2.17.

Folding both ends of nanowire into loop mirrors (i.e., Sagnac mirrors) is another way to form high quality microcavity, which was first demonstrated in glass nanowires (Wang et al., 2009). Xiao et al. (2011a) assembled Sagnac-loop mirror cavity using a CdSe nanowire (Figure 2.18), and realized mode selection for single-mode lasing operation.

2.5.4 Couplers and splitters

Due to the high fractional evanescent fields, photons inside a semiconductor nanowire can be efficiently coupled to photonic or plasmonic nanowires within near-field scale, which can be used for constructing a microscale optical coupler or splitter (Sirbuly et al., 2005; Guo et al., 2009; Xu et al., 2012b, 2012c).

Sirbuly et al. (2005) demonstrated evanescent coupling between different semiconductor nanowires. Huang, Yang, and Tong (2007) theoretically investigated the coupling efficiencies between two closely parallel nanowires with variant overlaps, and predicted that efficient coupling efficiency (as high as 90%) can be obtained under optimized circumstances. Xu et al. (2012b, 2012c) excited different semiconductor nanowires in a hybrid structure and reported the asymmetric light propagation inside

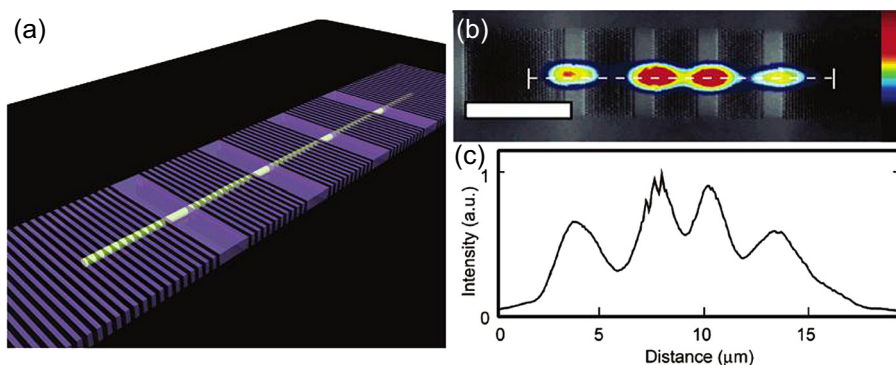


Figure 2.17 Hybrid nanowire-photonic-crystal cavity. (a) Schematic diagram of a CdS nanowire placed on a photonic crystal with engineered defects. (b) PL image (false color) and AFM image (gray scale) of a photonic-crystal-semiconductor-nanowire containing four defects. Scale bar: 5 μm . (c) Intensity of PL image in (b) taken along the nanowire axis. Figures adapted from Barrelet et al. (2006) with permission.

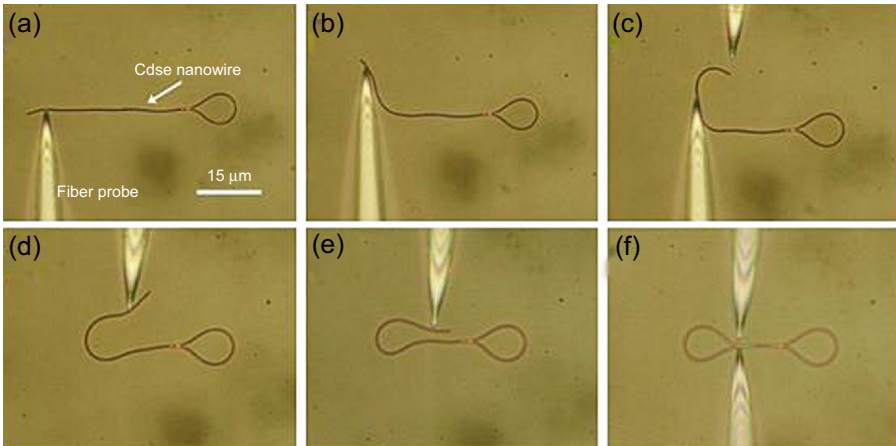


Figure 2.18 Optical micrograph shows the process of folding nanowire ends into loop mirrors by using tapered fiber probes.

Figures adapted from [Xiao et al. \(2011a\)](#) with permission.

branched nanowire structure combining with bandgap engineering in single semiconductor nanowire (as shown in [Figure 2.19\(a\) and \(b\)](#)). In 2009, benefiting from mode overlapping and end-face scattering for momentum compensation, [Guo et al. \(2009\)](#) reported coupling a ZnO nanowire and a Ag nanowire with efficiency as high as 80% ([Figure 2.19\(c–j\)](#)), and experimentally constructed a hybrid nanowire photon–plasmon splitter.

2.5.5 Optical modulator/switch

Optical switches are important building blocks in nanophotonic network ([Xu & Lipson, 2007](#); [Schonenberger et al., 2010](#); [Keil et al., 2011](#)). Nanowires offer unique advantages for optical switches due to their free-standing flexibility, ultrasmall dimension, and excellent waveguide properties.

[Barrelet, Greytak, and Lieber \(2004\)](#) reported modulation of propagating light intensity in a CdS nanowire by changing the electric field applied across the nanowire. With a similar design, [Greytak, Barrelet, Li, and Lieber \(2005\)](#) demonstrated electric field modulation of lasing emission in single CdS nanowire the next year (see [Figure 2.20](#)).

[Piccione, Cho, Van Vugt, and Agarwal \(2012\)](#) reported all-optical active switching in CdS nanowires. The switch was designed by etching a nanometer-scale gap into a CdS nanowire. A pulsed Ti:sapphire laser was used to excite the top nanowire to emit PL as probe light, while an Ar⁺ laser was used to pump the bottom nanowire to modulate the output light from the end face of the bottom nanowire. With Ar⁺ laser turned on, the probe light (2.510 eV) can be completely extinguished and a broader peak centered at 2.514 eV was enhanced. The stimulated scattering of excitons was suggested as the promising reason of the phenomenon.

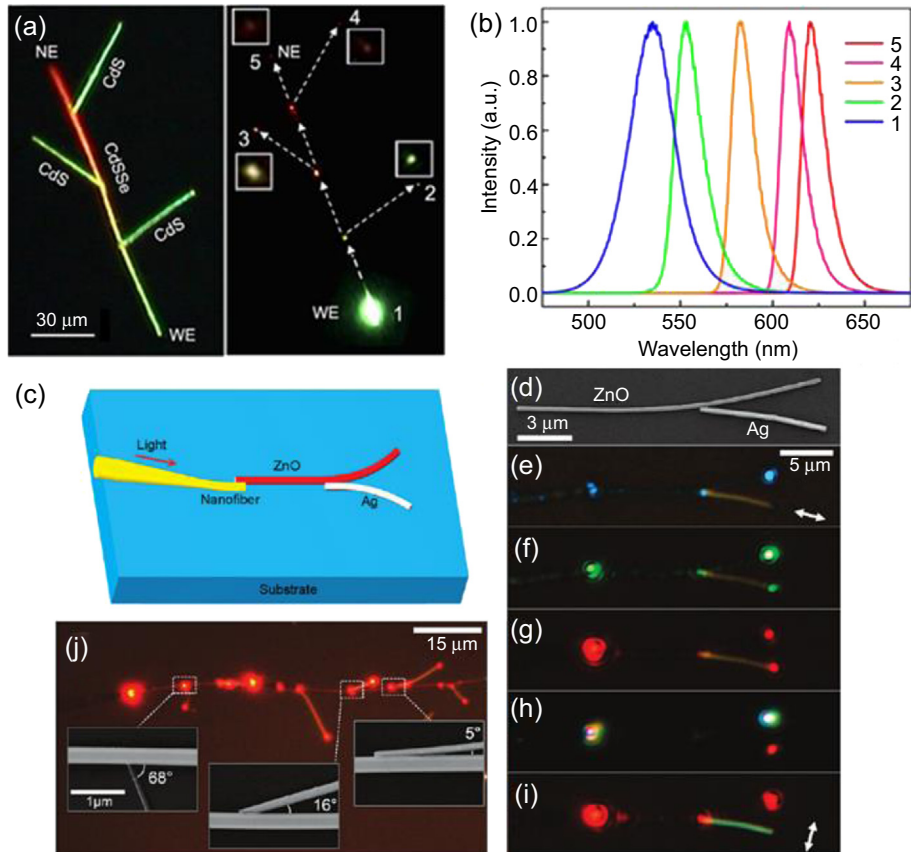


Figure 2.19 Branched nanowires structure. (a) PL image (left) under a diffused laser illumination and focused excitation (right) at nanowire end shown as point 1 of a branched nanowires structure consisted of CdS nanowires contacting with a composition-graded CdS_xSe_{1-x} nanowire (WE indicates wide bandgap end, NE indicates narrow bandgap end). The excited light at WE is coupled into three branches. (b) The PL spectra at output ends 1–5 shown in (a). (c) Schematic diagram of a hybrid coupler structure of ZnO nanowire and Ag nanowire. (d) SEM image of a typical hybrid coupler. (e–h) Optical micrographs of the hybrid coupler taken with a polarization parallel (as indicated by the white arrow) to the Ag nanowire. The coupler was excited by monochromatic lasers with wavelengths of 488, 532, 650 nm and white light from a halogen lamp, respectively. (i) Optical micrograph of the hybrid coupler taken with a polarization perpendicular to the Ag nanowire (excitation wavelength: 650 nm). (j) Optical micrograph of excitations of multiple Ag nanowires using a single ZnO nanowire. Inset shows the corresponding SEM images at the coupling regions.

Figure 2.19(a) and (b) adapted from Xu et al. (2012c). Figure 2.19(c–j) adapted from Guo et al. (2009) with permission.

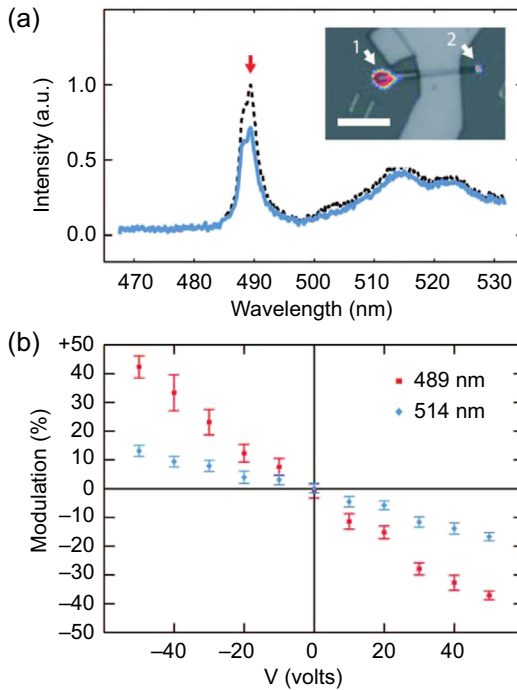


Figure 2.20 (a) Electric field-dependent CdS nanowire emission spectrum (dotted line indicates that the applied voltage is 0 V, solid line indicates that the applied voltage is 30 V). Inset: PL image of the structure, 1 indicates excitation site and 2 indicates observed site. Scale bar: 5 μm . Electric field-dependent modulation M is given by $(I_{\text{on}} - I_{\text{off}}) / I_{\text{off}}$, where I_{on} and I_{off} is the density of emitting light at the end of nanowire with and without applied voltage, V . Figures adapted from [Gretyak et al. \(2005\)](#) with permission.

2.6 Nanowire photoluminescence and lasers

2.6.1 Introduction

As active nanowaveguides with high gain, semiconductor nanowires provide an ideal platform for generation, waveguiding, amplification, and lasing oscillation of PL emission on nanoscale. While pumped optically or electrically, lasing can be readily obtained inside these nanowires with feedback either from end-face reflections or near-field scatterings, with unique features such as miniaturized footprints and high flexibilities. Meanwhile, the rich family of II–VI semiconductors offers nanowire lasers with broad spectral operation ranging from UV to near IR. Recently, nanowire lasers have been attracting worldwide attention on a variety of topics such as signal processing, optical sensing, on-chip communications, and quantum optics.

Here we first review the current developments and perspectives of II–VI semiconductor nanowire lasers. Specifically, we will introduce principles and basic types of

nanowire lasers based on F-P cavities, followed by nanowire plasmon lasers, tunable lasers, and single-mode lasers.

2.6.2 Principles of semiconductor nanowire lasers

As an active nanowaveguide with high gain and optical recirculation for positive optical feedback, II–VI semiconductor nanowire is an ideal nanostructure for nanolaser. To establish the lasing operation, a proper pumping process is necessary to excite the excitons to realize population inversions, thus photons within a certain narrow spectral range will be amplified coherently inside the active nanowires. When the feedback provided by the cavity is strong enough, the lasing oscillation can be established, resulting in a nanowire laser.

The first lasing action in nanowire was demonstrated in 2001 in ZnO nanowires (Huang et al., 2001a). Since then, II–VI semiconductor nanowires lasers have attracted intensive attention (Dasgupta et al., 2014; Xia et al., 2003; Yan, Gargas, & Yang, 2009; Zimmmler, Capasso, Müller, & Ronning, 2010). So far, lasing in semiconductor nanowires across the UV, visible, and near-IR spectral regions has been reported by materials such as ZnO (3.37 eV) (Gargas, Toimil-Molares, & Yang, 2009; Gruzintsev et al., 2010; Johnson et al., 2003; Van Vugt et al., 2006; Yan et al., 2003a; Yang et al., 2002; Zhang, Russo, & Mao, 2005; Zimmmler, Bao, Capasso, Müller, & Ronning, 2008), ZnS (3.7 eV for hexagonal-wurtzite phase and 3.68 eV for cubic phase) (Xiong et al., 2004a; Ding et al., 2004; Chen et al., 2010), CdS (2.42 eV) (Agarwal, Barrelet, & Lieber, 2005; Pan et al., 2005a, 2007; Greytak et al., 2005; Cao et al., 2007; Liu et al., 2011; Geburt et al., 2012), and CdSe (1.74 eV) (Li et al., 2013b; Xiao et al., 2011a, 2011b).

An issue noted within the context of lasing is the ASE (Ma et al., 2013; Samuel, Nanddas, & Turnbull, 2009; You et al., 2013; Zhu et al., 2008; Zimmmler et al., 2008). ASE occurs when the photons emitted by spontaneous emission are optically amplified by the process of stimulated emission as passing through the gain material (Zhu et al., 2008). It is different from general laser in the absence of strong feedback applied by optical cavities, resulting in exhibiting only part of the properties of general laser. The properties of emitting light transiting from ASE to laser oscillation in ZnO nanowires has been carefully investigated (Zimmmler et al., 2008), as shown in Figure 2.21. In ASE process, longitudinal modes appear gradually as population inversion starts building up (Zimmmler et al., 2010). The output power of the nanowire exhibits a superlinear relationship with pump intensity different from spontaneous emission and lasing process (see Figure 2.21(c)).

2.6.3 Plasmonic laser

Nanoscale plasmonic nanowire lasers, as coherent radiation at optical frequency, have been intensively investigated, with unique features especially regarding their operation beyond the classical diffraction limit. Benefiting from its high optical gain, II–VI semiconductor nanowire can be coupled with a metallic nanostructure for realizing plasmonic lasing oscillation.

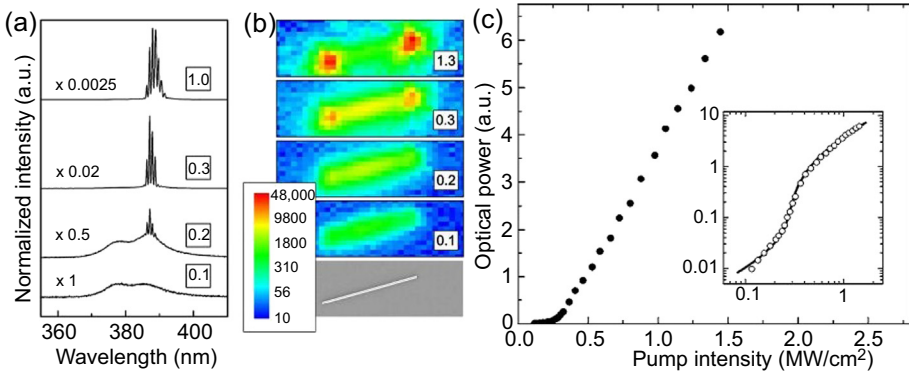


Figure 2.21 Transition from spontaneous emission to lasing oscillation in single ZnO nanowire. (a) Output spectrum with pump power increasing gradually. (b) CCD and SEM images of the same nanowire in (a). (c) Pump power-dependent output laser intensity. Inset: a log–log scale for the same data.

Figures adapted from [Zimmler et al. \(2008\)](#) with permission.

In 2009, by coupling a CdS nanowire with a Ag film, [Oulton et al. \(2009\)](#) realized plasmonic laser in a nanowire-surface hybrid structure with a mode area as small as $\lambda^2/400$. [Wu et al. \(2013\)](#) demonstrated a hybrid photon-plasmonic laser by longitudinal coupling of CdSe nanowire and Ag nanowire (see [Figure 2.22](#)), which separated a pure plasmonic cavity mode from the photonic mode. Very recently, by locating triangular GaN nanowire on Al film with a spacer layer of SiO₂, [Zhang et al. \(2014b\)](#) demonstrated a room temperature UV plasmonic laser. In the plasmonic devices, the ohmic losses and scattering/radiation losses are efficiently

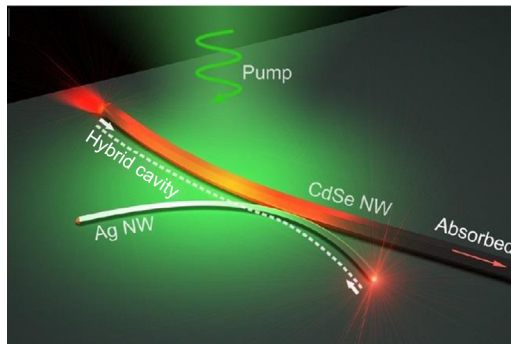


Figure 2.22 Schematic diagram of a coupled hybrid cavity consisting of a CdSe nanowire and a Ag nanowire.

Figure adapted from [Wu et al. \(2013\)](#) with permission.

suppressed through reducing the surface roughness of the metal and SiO₂; meanwhile, the gain-compensation is greatly enhanced because of the flat metal–insulator–semiconductor interface.

2.6.4 Tunable lasers

As mentioned before, bandgap engineering of alloyed II–VI semiconductor nanowires can be realized by fabrication and thus can be readily used for tuning lasing wavelength (Liu et al., 2005, 2007; Luan et al., 2012; Pan et al., 2005b, 2006, 2009; Xu et al., 2012a; Zapien et al., 2007).

Liu et al. (2005) reported a wavelength-controlled nanowire laser with Zn_xCd_{1–x}S nanoribbons. The lasing emission of 485–515 nm and 340–390 nm was realized by controlling the composition x . In the same year, Pan et al. (2005b) realized lasing wavelength tuning of 508–705 nm with CdS_xSe_{1–x} nanobelts.

On a single-nanowire scale, by looping a CdSe nanowire into a tunable loop mirror cavity, Xiao et al. (2011a) reported a 7-nm tuning of lasing wavelength within a single CdSe nanowire laser (see Figure 2.23(b)). By combining the bandgap engineering and cavity parameters, Liu et al. (2013d) demonstrated lasing emission at two different colors (with the wavelength separation of 107 nm) simultaneously in a single bandgap graded CdS_xSe_{1–x} nanowire (see Figure 2.23(c–e)). By looping one wide bandgap end of the nanowire, two relatively isolated cavities were formed, providing lasing oscillations at two different wavelengths. The total output color can be continuously tuned by changing the relative pumping powers of the two cavities.

2.6.5 Single-mode nanowire lasers

Without intrinsic mode selection capability, semiconductor nanowire lasers generally exhibit multimode lasing behaviors. Previously, fabricating of distributed Bragg reflector (DBR) mirrors on the nanowires was proposed to obtain single-mode nanowire laser (Zhang & Loncar, 2008). However, the difficulty in DBR fabrication and the degradation of nanowire exposed to ion beams prevents its experimental realization. Another possible approach to realize single-mode lasing is to expand the free-spectral range by reducing the length of nanowire cavity, however, this will inevitably increase the lasing threshold of the nanowire laser and require significantly higher pumping intensity (Zimmler et al., 2008).

Xiao et al. (2011a) reported a single-mode single-nanowire laser by folding the ends of a CdSe nanowire into loop mirrors to generate additional lasing cavities (Figure 2.24(a)). Based on the Vernier effect of the coupled multiple cavities for mode selection, a single-mode nanowire laser with low threshold was realized experimentally. Shortly after, the same group demonstrated a single-mode lasing in an X-type cavity consisting of two coupled CdSe nanowires (Figure 2.24(b) and (c)) (Xiao et al., 2011b).

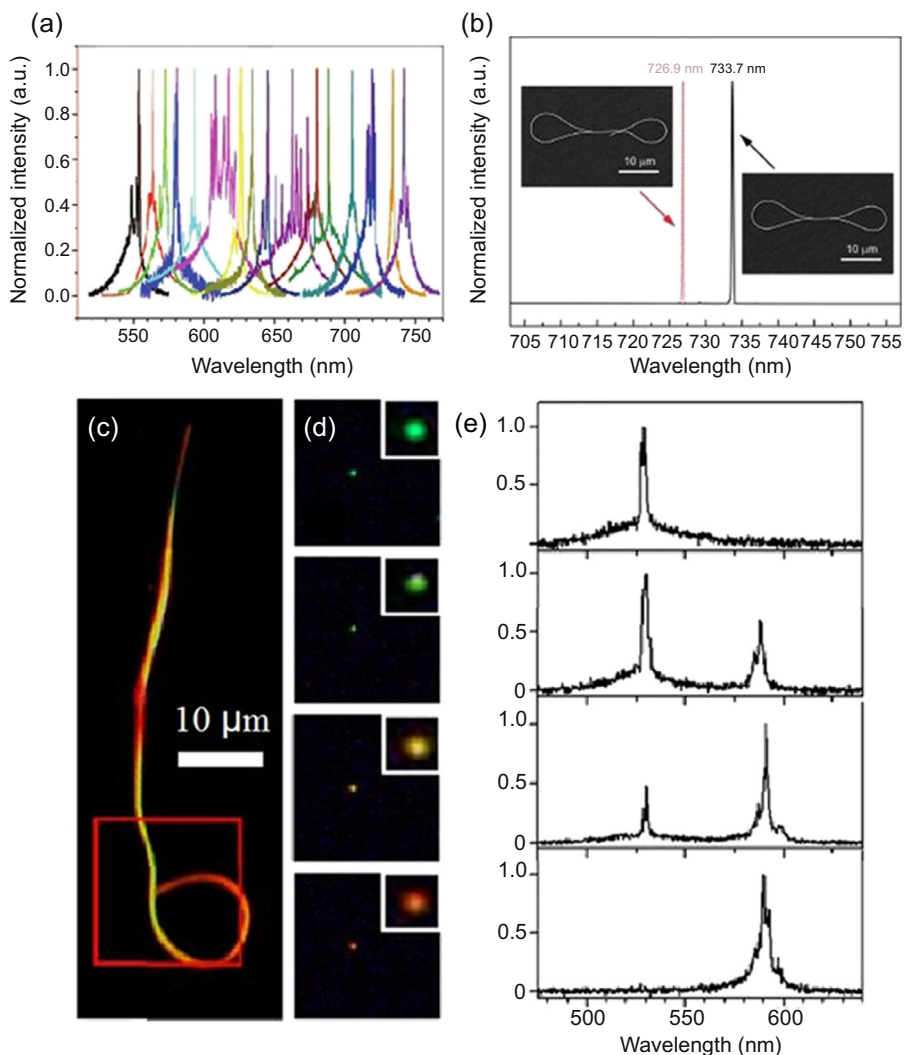


Figure 2.23 Nanowire tunable lasers. (a) Wavelength tuning in a single nanowire laser. Spectrum of the single-mode lasing shifts with changing of the geometry of the loop. (b) Spectrum collected from different positions along the spatially composition-graded CdS_xSe_{1-x} nanowires. (c) Dark-field image of a CdS_xSe_{1-x} nanowire with one end of the nanowire looped. (d) Real color images of the laser with different pumping power for the two cavities (taken from the red box in the left image). (e) Normalized spectrum of the laser with different pumping power for the two cavities.

Figure 2.23(a) adapted from Pan et al. (2009). Figure 2.23(b) adapted from Xiao et al. (2011a).

Figure 2.23(c–e) adapted from Liu et al. (2013d) with permission.

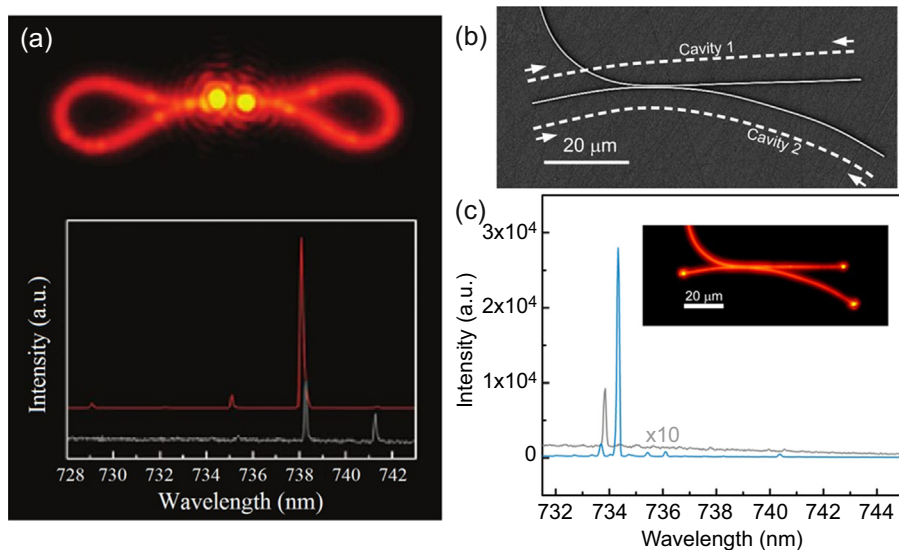


Figure 2.24 Single-mode nanowire lasers. (a) PL image (upper) and lasing spectrum (under) of the single-mode laser based on a single CdSe nanowire. (b) SEM image of a cavity consisting of two X-coupled CdSe nanowires. (c) Single-mode lasing spectrum of the X-coupled cavity. Inset: PL image of the structure.

Figure 2.24(a) adapted from Xiao et al. (2011a). Figure 2.24(b) and (c) adapted from Xiao et al. (2011b) with permission.

2.7 Conclusions and outlook

In summary, we have provided an outline and brief highlights of prominent research activities over the past two decades in the emerging field of the optical properties of II–VI compound semiconductor nanowires, and their applications in nanophotonics. The vast progress achieved from fundamental understanding to practical applications will continue to drive the entire material research community. An important avenue for further research is to integrate more basic physical phenomena (such as from optical, electronic, magnetic, thermal, and mechanical aspects) for constructing more complex but integrated systems with multifunctionality.

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Advanced III–V nanowire growth toward large-scale integration

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Several elaborate reviews on the properties of III–V nanowires (NWs) already exist in the literature (Hyun, Zhang, & Lauhon, 2013; Joyce et al., 2011; Lapierre et al., 2013; Soci et al., 2010; Yan, Gargas, & Yang, 2009); here we focus on the specific issue of large-scale integration, which we believe is of paramount importance to enable transition from the initial research and development phase to practical implementation of these unique systems and devices. Selective-area growth of ordered, vertical nanowire arrays and 3D structure from patterned locations, and the corresponding functional devices, will be discussed.

3.1 Synthesis of III–V NWs

Bottom-up growth offers a great freedom in fundamental study of NWs with extremely small diameters, excellent surface morphology, complex structures, and controllable crystallographic structures, enabled by precise control of growth mechanisms and techniques.

3.1.1 Growth mechanisms

During the last two decades, the growth of III–V NWs has been extensively studied. Diverse growth mechanisms of these 1D materials have been proposed among the research community. For the sake of discussion, we will broadly categorize growth mechanisms into two groups: (1) the vapor-phase mechanisms, which encompass vapor–liquid–solid (VLS), vapor–solid–solid (VSS), vapor–solid (VS), oxide-assisted growth (OAG), and self-catalytic growth (SCG); and (2) the catalyst-free selective-area (SA) growth. These growth mechanisms will be reviewed in the following sections, with particular attention paid to the controversies regarding applicability of the different vapor-phase models.

All the vapor-phase mechanisms require a catalyst M for NW growth. As shown in the dotted inset of Figure 3.1(a), M can be composed of (1) a non-III metal alloying with a group-III element ($M_x\text{III}_y$) that characterizes a VLS growth, (2) a multigrain M for VSS, (3) an oxide for OAG, or (4) a III element for SCG. The major role of M is to lower the nucleation energy of a III–V layer at the seed/substrate interface, promoting growth of NWs.

The surface free energy at the seed/substrate interface determines the crystal growth direction of the NWs. III–V NWs can present pure cubic zinc blende (ZB), pure

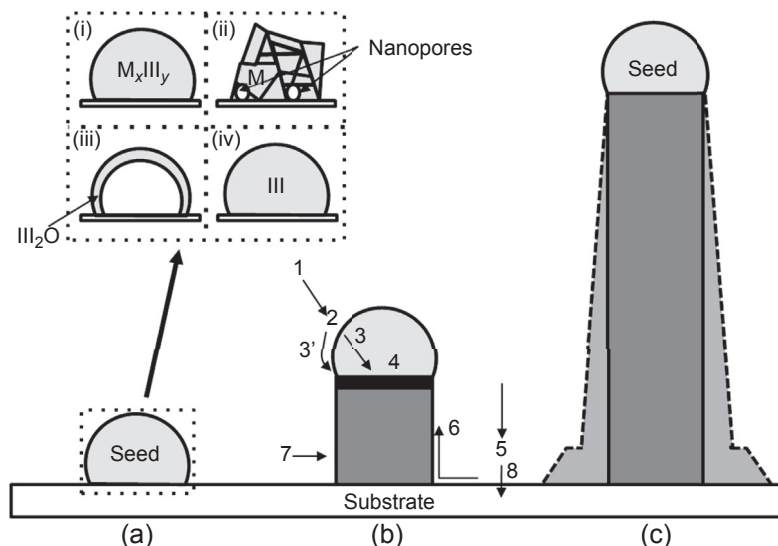


Figure 3.1 Scheme of NW growth mechanism process. (a) Formation of the seed with the different compositions (dotted inset): (i) alloyed M_xIII_y (VLS), (ii) multigrained (VSS) with possible nanopores (VQS), (iii) oxide-assisted III_2O or SiO_x (OAG), and (iv) III group element (SCG). (b) NW growth and the involved physical and chemical processes: (1) gas-phase diffusion, (2) dissociation reactions on the seed or on the NW surface, (3) diffusion of reactants through the seed or (3') along the seed to the seed/NW interface, (4) the formation of the semiconductor crystal at the liquid–solid interface (ledge) (Borgström, Verheijen, Immink, Smet, & Bakkers, 2006), (5) adsorption of precursor molecules on the substrate or NW surface, (6) surface diffusion, (7) crystal growth on the NW sidewall, and (8) film growth on the substrate surface. Steps 2, 4, 7, and 8 are activated processes, which depend exponentially on the temperature. (Adapted with permission from Verheijen, Immink, De Smet, Borgström, and Bakkers (2006). Copyright 2006, American Chemical Society.) (c) As-grown NW with straight or tapered (dashed lines) morphologies.

hexagonal wurtzite (WZ) or mixed crystal structures. For ZB NWs of relatively larger diameter, the preferred growth orientation is $\langle 111 \rangle$ due to the lower Gibbs free energy of nucleation for a $\langle 111 \rangle$ oriented NW with $\{110\}$ or $\{112\}$ facets (Schmidt, Senz, & Gösele, 2005) compared to $\langle 110 \rangle$ and $\langle 112 \rangle$ that are commonly observed at smaller diameters (particularly sub-20 nm diameters in Ge and Si (Dayeh & Picraux, 2010)). The $\{111\}$ substrate can possess either a cation (group-III) terminated surface known as (111)A or an anion (group-IV) terminated surface known as (111)B and the latter is more commonly used than the former in NW growth. In contrast to bulk arsenide and phosphide III–V materials, arsenide and phosphide NWs can crystallize in WZ orientation due to high levels of supersaturation and strong influence of NW facets on nucleation energies, where WZ facets have lower energies than those for ZB (Glas, Harmand, & Patriarche, 2007). Table 3.1 summarizes growth directions, types of substrates, growth mechanisms, and occurrence of crystallographic defects, such as stacking faults (SFs), twin planes, and polytypism (alternation of ZB and WZ segments) in binary III–V NWs reported in the literature.

Table 3.1 Commonly observed growth directions and cross-sections for some III–V NWs. The listed references are not exhaustive

Material	Growth direction	Growth substrate	Growth mechanism	CSG ^a	SF ^b	PT ^c	References
GaAs	$\langle 111 \rangle B / [0001]$	GaAs(111)B	VLS, SA		Yes	Yes	Hiruma et al. (1995)
	$\langle 110 \rangle$	GaAs(001)	VLS		No	No	Fortuna et al. (2008), Ghosh, Kruse, and Lapierre (2009), and Mikkelsen, Sköld, Ouattara and Lundgren (2006)
	$\langle 110 \rangle$	GaAs(100)	VLS		No	No	Wu et al. (2003)
	$\langle 112 \rangle$		VLS				Givargizov (1975)
	$\langle 100 \rangle$	Si(111)	VLS		No	No	Ihn, Song, Kim, and Yong Lee (2006)
	$\langle 111 \rangle A$	GaAs(111)A	VLS		No	No	Wacaser, Deppert, Karlsson, Samuelson, and Seifert (2006)
InP	$\langle 111 \rangle B / [0001]$		VLS		Yes	Yes	Duan, Huang, Cui, Wang, and Lieber (2001)
	$\langle 110 \rangle$	InP(110)	SCG		No		Mattila, Hakkarainen, Jiang, Kauppinen, and Lipsanen (2007)
	$\langle 100 \rangle$	InP(001)	VLS				Krishnamachari et al. (2004)
InAs	$\langle 111 \rangle B / [0001]$	GaAs, InAs(111)B	VLS, SA		Yes	Yes	Hiruma et al. (1995)
	$\langle 100 \rangle$	InAs(001)	VLS, (VSS)				Seifert et al. (2004)
	$\langle 110 \rangle$	InAs(001)	VLS, (VSS)				Seifert et al. (2004)
	$\langle 112 \rangle$	InAs(111)B	VLS				Zhang, Zou et al. (2009)

Continued

Table 3.1 Continued

Material	Growth direction	Growth substrate	Growth mechanism	CSG ^a	SF ^b	PT ^c	References
GaP	$\langle 111 \rangle$ B		OAG		Yes	No	Liu et al. (2005)
	$\langle 111 \rangle$ B	Si(111)	VLS		Yes	No	Tateno, Hibino, Gotoh, and Nakano (2006)
GaSb	$\langle 110 \rangle$	Si(111)	OAG		Yes	No	Shi, Zheng, Wang, Lee, and Lee (2001)
	$\langle 111 \rangle$ B	GaAs(111)B	VLS		No	No	Jeppsson, Dick et al. (2008) and Jeppsson, Dick, Wagner et al. (2008)
	$\langle 110 \rangle$		VLS		No	No	Vaddiraju et al. (2007)
	$\langle 110 \rangle$		VLS		No	No	Pendyala et al. (2010)
InSb	$\langle 111 \rangle$ B	InSb(111)B	VLS			No	Gutsche et al. (2012) and Lugani et al. (2012)
	$\langle 220 \rangle$	InSb(111)B	VLS				Gutsche et al. (2012) and Lugani et al. (2012)
	$\langle 111 \rangle$	InSb(-1-1-1)B	VLS		Yes	No	Vogel, De Boor et al. (2011)
	$\langle 111 \rangle$	InP(111)B	VLS		No	No	Plissard et al. (2012)
	$\langle 110 \rangle$	InSb(111)	VLS		No	No	Park, Prokes, Twigg, Ding, and Wang (2007) and Paul et al. (2010)

^aCross-sectional geometry.^bStacking faults.^cPolytype.Adapted with permission from [Fortuna and Li \(2010\)](#). Copyright 2010, IOP Publishing.

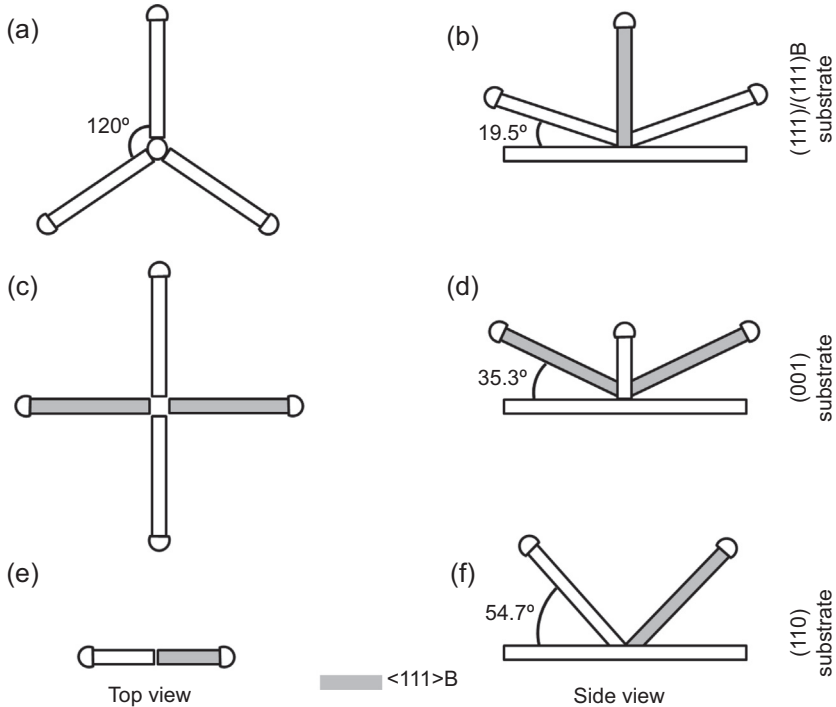


Figure 3.2 Schematic illustration of $\langle 111 \rangle$ NWs grown epitaxially on several substrates with different orientations. Both elemental and compound semiconductor substrates are combined into the same illustrations with $\langle 111 \rangle$ B direction specified via gray shading of the NW. Adapted with permission from [Fortuna and Li \(2010\)](#). Copyright 2010, IOP Publishing.

Figure 3.2 illustrates out-of-plane $\langle 111 \rangle$ growth direction on (111), (110), and (001) substrates, showing different angles relative to the substrates as well as various azimuth between NWs. NWs growing perpendicular to the substrate are only observed in [Figure 3.2\(a\) and \(b\)](#) with $\langle 111 \rangle$ B growth direction on (111)B substrate. Such growth is energetically favorable, which promises application of III–V NWs in vertically aligned NW array devices. On (001) substrate, NWs normally grow in four $\langle 111 \rangle$ directions with 90° between one another, as shown in [Figure 3.2\(c\) and \(d\)](#). Exceptionally, aligned planar $\langle 110 \rangle$ NWs grown on GaAs(001) substrate have also been achieved through the modulation of growth temperature ([Fortuna, Wen, Chun, & Li, 2008](#)). On (110) substrate, two $\langle 111 \rangle$ directions are azimuthally separated by 180° ([Figure 3.2\(e\) and \(f\)](#)).

VLS is the most common growth mechanism describing the NW growth. This model was first introduced to describe the growth of Si nanowhiskers ([Wagner & Ellis, 1964](#)), where the elongation of the Si nanowhiskers is driven by the continuous supersaturation inside the eutectic liquid seed by absorbing gaseous precursors. The diameter of these wires is mainly determined by the size of the catalysts. A handful of M can be used to mix with a single III element to form the right $M_x\text{III}_y$ alloy seed ([Nguyen, Ng, & Meyyappan, 2005](#)). The most common catalyst is Au, since it can form many stable eutectic alloys with the different III elements—for example, AuGa ([Harmand](#)

et al., 2005), AuIn (Lee, Wang, & Matijasevic, 1993). The shape, size, and composition of the alloy seed are determined by the growth conditions including the annealing temperature, the growth time, and the chamber environment (Harmand et al., 2005). Note that NWs can only grow when the temperature is above the alloy eutectic point in the VLS growth regime.

Below the eutectic temperature, the M_xIII_y alloy is not stable and VLS should not occur. However, many groups reported growths below the eutectic point (Persson, Larsson et al., 2004; Persson, Ohlsson, Jeppesen, & Samuelson, 2004), for example, GaAs and InAs with Au catalysts (Dick et al., 2005). With the help of X-ray energy-dispersive spectrometer and 3D model simulations (based on mass transfer and chemical reaction kinetics equations), Persson et al. demonstrated that in the absence of any growth precursors on a transmission electron microscope (TEM) heating stage, the catalyst stayed in solid-phase at temperatures that are comparable to the growth temperature of GaAs NWs and the growth was proposed to follow the VSS growth mechanism. Recent *in situ* TEM studies have shown that the bulk-phase diagram cannot be used to explain NW growth due to liquidus line suppression and lowering of the eutectic temperature (Sutter & Sutter, 2010). In addition, the presence of a low partial pressure of the input reactant can substantially lower the metal-reactant eutectic temperature by over 120 °C (Gamalski, Tersoff, Sharma, Ducati, & Hofmann, 2010), substantiating the universal applicability of the VLS mechanism at deep sub-eutectic temperatures. (Figure 3.1(a)(ii) and Figure 3.3(b)), based on solid-phase diffusion. In principle, the growth rate of VSS should be low for different reasons: (1) the diffusions of the III, V elements to the interface seed-substrate or seed-NW (i.e., the ledge, Figure 3.1(b)(3')) are very slow; and (2) the solubility of the V elements inside the seed is very low. It was estimated that the growth rate for VSS was 100 times lower in magnitude than for VLS (Kodambaka, Tersoff, Reuter, & Ross, 2007) accompanied with a significant taper (sidewall growth) of the NW. However, by comparing the growth rate for GaAs, InP, or InAs NWs under diverse growth mechanisms reported in the literature (Dayeh, Yu, & Wang, 2007d; Dick et al., 2005; Novotny & Yu, 2005; Persson, Fröberg, Jeppesen, Björk, & Samuelson, 2007; Tchernycheva et al., 2007) and summarized in Table III of Mohammad (2009), the growth rates under VSS and VLS are quite equivalent. As suggested by Mohammad et al., and despite the different proposed growth modes, the growth rates are similar. Mohammad postulated that the VSS growth of III–V NWs does not follow a standard VSS mechanism but a vapor–quasisolid–solid mechanism (VQS).

A solid alloy seed characterizes VQS with presence of semimolten nanopores (Figure 3.1(a)(ii)). The nanopores are formed by the transition phase (solid to liquid), lowering thus the activation energy by many parameters, that is, contaminants inside the chamber, inside the alloy seed, at the interface between the seed and the substrate or the seed and the NW, and the solubility of M in III (or vice-versa). Small diameter as-grown GaAs NW presents a solid Au tip (extremely low solubility of Ga in Au because of the Gibbs–Thomson effect (Givargizov, 1975)), while thicker NW exhibits an AuGa₂ alloy tip (Dayeh, Chen et al., 2008).

Instead of using a noble metal as a catalyst to induce the nucleation and the growth of the NWs, a semiconductor-oxide or metal-oxide can also be used to assist the

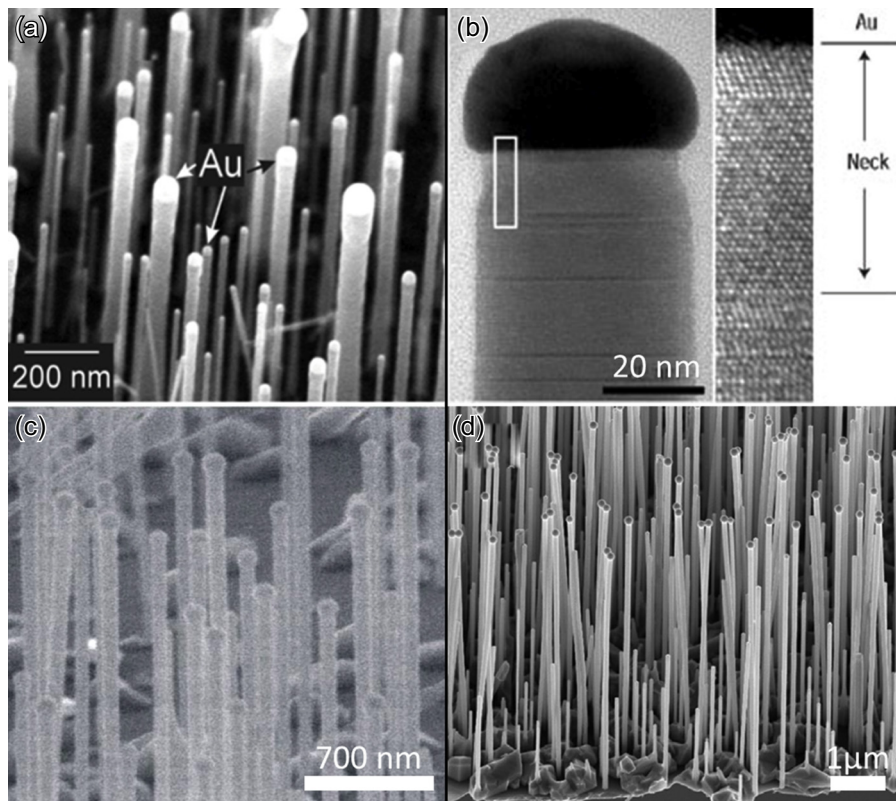
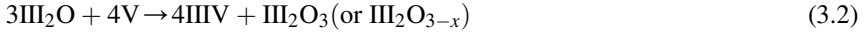


Figure 3.3 Electron microscope images of NWs grown by vapor-phase mechanisms. (a) InP NWs by VLS. (Reprinted with permission from Bhunia, Kawamura, Fujikawa, Tokushima, and Watanabe (2004). Copyright 2004 with permission from Elsevier.) (b) GaAs NWs by VSS. (Reprinted with permission from Persson, Larsson et al. (2004). Copyright 2004 Nature Publishing Group.) (c) GaP NWs by OAG. (Reprinted with permission from Fontcuberta I Morral, Colombo, Abstreiter, Arbiol, and Morante (2008). Copyright 2008 AIP Publishing LLC.) (d) InP NWs by SCG. (Reprinted with permission from Dheeraj et al. (2013). Copyright 2013, Elsevier.)

synthesis (Figure 3.1(a)(iii)). This OAG mechanism was first introduced by Zhang et al. to explain the growth of Si NWs through SiO₂-assisted vapor-phase reaction at high temperature (Zhang, Lifshitz, & Lee, 2003), which has a similar growth rate compared to the VLS mechanism. OAG is a process that can be also applied to grow InP NWs and nanotubes: a powder mixture of (InP:In₂O₃) is heated at a high temperature (~ 1150 °C) in a conventional tube furnace, which allows the formation of InP NWs/nanotubes at the cold part of the furnace (~ 500 – 600 °C). By tuning the ratio of In₂O₃ in the initial powder mixture, one can modify the ratio of nanotubes and nanowires synthesized, but also tune the morphological characteristics of such nanostructures (Tang, Bando, Liu, & Golberg, 2003). OAG is also reported for the synthesis of GaP NWs via a laser-ablated target of GaP and Ga₂O₃ (Shi et al., 2001),

InAs NWs, and GaAs (Fontcuberta I Morral, Colombo, et al., 2008) (Figure 3.3(c)) NWs via the assistance of a thin layer of SiO_x that assists in creation of steps on the substrate surface that lower the nucleation energy for NW growth by a group-III growth seed. For III–V NWs, the vapor transport process is accompanied by an oxidation–reduction process and can be described as follows:



The catalyst M (here as a metal-oxide III_2O_3) and the alloy seed (also an oxide III_2O) are not fully solid and are composed of semimolten nanopores, similar to the cases of VSS and VQS.

In addition, SCG can occur when group-III elements act as M (Figure 3.1(a)(iv)). Instead of introducing extrinsic catalysts, intrinsic group-III elements provided by the surface reconstruction of the III–V substrate via a pre-annealing step can assist the synthesis. For instance, Novotny et al. reported the SCG growth of InP NWs using metal organic chemical vapor deposition (MOCVD) with TmIn and PH_3 precursors under In-rich growth conditions (Figure 3.3(d)). Heterogeneous reactions and supersaturation in the liquid droplet led to nucleation of NW growth. By varying the growth conditions from In-rich to In-deficient conditions, the NW density and their taper was controlled (Novotny & Yu, 2005).

NWs grown on a substrate patterned with arrays of metal catalyst enable the precise control of diameters and lengths. Such ordered growth provides a way to characterize synergetic effect, which is a technological challenge for repeatability criterion. It was observed by Borgström et al. on GaP NWs grown by MOCVD (Borgstrom, Immink, Ketelaars, Algra, & Bakkerserik, 2007) that the growth rate increased with decreasing distance between NWs. This effect originates from the better decomposition of the precursors (i.e., TMGa) by an increase of the surface collection area when the wire–wire spacing is reaching an optimum value, which is a competition between the Gibbs–Thomson effect and surface diffusion-limited growth.

Catalysts exist in the growth mechanisms discussed above. Metal catalysts are widely used for VLS and VSS growths; however, they usually act as unintentional impurities and form deep-level traps inside the NWs, degrading their electrical and optical properties. Moreover, catalyst instabilities, for example, diffusion of catalyst along the NW, can induce defects on the NW or extra growth on NWs (nanotrees).

Alternatively, catalyst-free SA growth enables the NW growth in well-defined locations without introducing any extrinsic catalysts. This method relies on a patterned thin SiO_2 layer with small openings defined by the combination of e-beam lithography and wet (or dry) etching covering the III–V substrate (Figure 3.4(a) top). It was developed in the early 1960s for Si layer growth (Joyce & Baldrey, 1962) and then transferred to the growth of III–V micropillar arrays (Hamano, Hirayama, & Aoyagi, 1997; Motohisa, Noborisaka, Takeda, Inari, & Fukui, 2004; Motohisa, Takeda, Inari, Noborisaka, & Fukui, 2004). Several groups investigated the role of the different growth parameters in the SA technique. Hamano et al. observed the growth rate

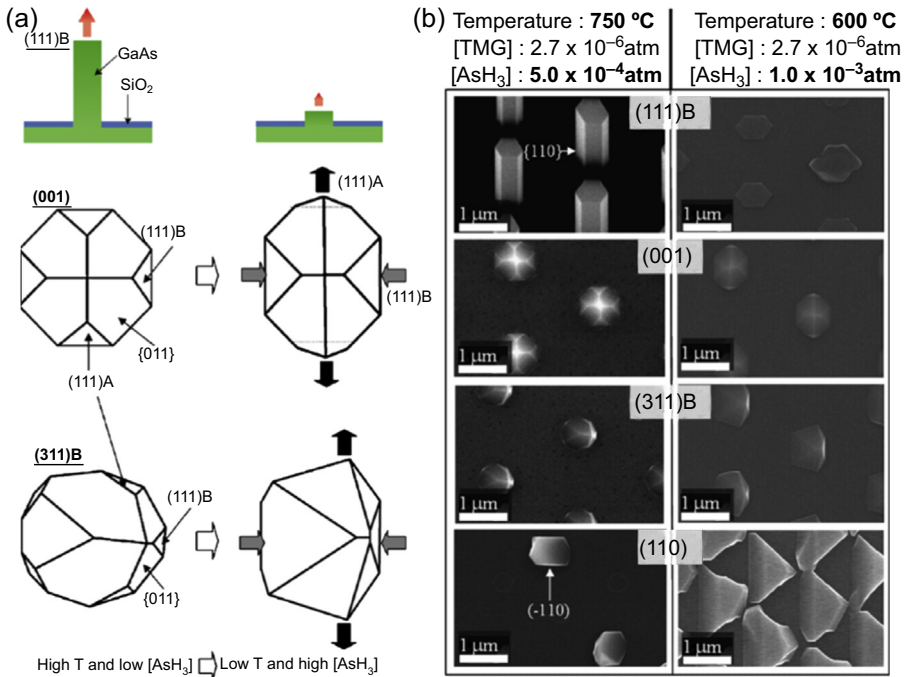


Figure 3.4 (a) Schematics of grown structures on (111)B, (001), and (311)B under growth condition A (high T_G and low $[\text{AsH}_3]$ (flow rate) condition, left) and B (low T_G and high $[\text{AsH}_3]$ condition, right). (b) Tilted and top view SEM images of GaAs grown on (111)B, (001), (311)B, and (110) substrates. The images in the left column summarize the structure grown under high T_G and low $[\text{AsH}_3]$ condition, while those in the right column stand for the growth under low T_G and high $[\text{AsH}_3]$ condition.

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increased as the radius decreased and the GaAs micropillars with a hexagonal cross-section with smooth (-110) facets were formed during the growth on (111)B GaAs substrate. Ikejiri et al. reported an advanced study of GaAs NW growth on substrates with different orientations and growth conditions ([Ikejiri, Noborisaka, Hara, Motohisa, & Fukui, 2007](#); [Ikejiri et al., 2008](#)). As-grown GaAs NWs exhibited low index facets, and their growth rate was mainly determined by the growth parameters ([Figure 3.4](#)), that is, flow rate of AsH_3 , growth temperature and substrate crystal orientation.

It is of great importance to integrate NWs into the existing Si-technology platform in order to implement devices with novel functionalities. Despite the controversies about the vapor phase mechanisms, that is, the seed nature, VLS-grown vertical NWs are shown to be the best candidates for their integration in an Si platform.

3.1.2 Growth apparatus

Numerous growth methods have been developed to grow semiconductor-based thin films, and each method is dedicated to a specific application (e.g., light-emitting diodes

with MOCVD or quantum cascade lasers with molecular beam epitaxy (MBE)). Various techniques are also implemented in III–V NW growth: highly controllable methods including MOCVD, MBE, chemical beam epitaxy (CBE); and less controllable techniques such as chemical vapor deposition (CVD), laser-assisted catalytic growth (LCG), pulse laser ablation, and wafer annealing.

The first NW growth was realized on Si in 1964, where Si whiskers were grown on a halide saturating system (Theuerer, 1961) through the H_2 reduction of silicon tetrachloride ($SiCl_4$) precursor via the VLS mechanism (Wagner & Ellis, 1964), while the first III–V NW with well-understood growth mechanism was reported in the late 1990s. Hamano et al. selectively grew GaAs pillars with a submicron diameter using MOCVD (Hamano et al., 1997). In the late 1990s and early 2000s, NWs started to arouse interests and were extensively developed. Lieber et al. reported the growth of Si and Ge NWs through laser ablation and the VLS mechanism (Morales & Lieber, 1998). This technique consists of the pulsed laser ablation of a target containing the NW elements and the metal catalyst, followed by the condensation of the vapors into nanometer-sized clusters and NW growth via VLS. This technique was also implemented in the growth of III–V systems, for example, GaAs NWs (Duan, Wang, & Lieber, 2000), InP NWs (Duan et al., 2001; Gudiksen, Wang, & Lieber, 2001; Wang, Gudiksen, Duan, Cui, & Lieber, 2001), and GaAs/GaP heterostructure NWs (Gudiksen, Lauhon, Wang, Smith, & Lieber, 2002). However, it is limited by the availability of target sources and the absence of control of the NW position on the substrate.

MOCVD, also known as organic metallic vapor phase epitaxy (OMVPE) or MOVPE, is a growth process allowing the synthesis of single, polycrystalline, or amorphous material layers. The liquid precursors are metal-organic compounds, for example, trimethyl indium ($(CH_3)_3In$, TMIIn), tertiarybutyl arsine (TBAs), etc. (Figure 3.5(a)). After being introduced into the chamber, the precursors are decomposed through pyrolysis, enabling III and V atomic elements to bond to the surface of the heated substrate and form an epitaxial crystalline layer. This method was first developed in the late 1960s (Manasevit, 1968), though MOCVD-like fragments were patented in the early 1960s (Miederer, Ziegler, & Dotzer, 1962, 1963). MOCVD is considered as the most versatile, robust technique to grow various kinds of semiconductor materials (III–V, II–VI), with an excellent uniformity on a large scale and a high growth rate. The capability of forming an abrupt interface and selective epitaxial growth has made MOCVD one of the most appreciated and economical techniques for diverse industrial applications like LEDs, injection lasers (near IR-blue), solar cells, high-speed transistors, and photonic integrated circuits. It is of great importance to note that the quality of growth strongly depends on the growth conditions. Investigations have been made from homoepitaxy (i.e., on lattice-matched substrate) to heteroepitaxy (i.e., on Si substrates) (Mårtensson et al., 2004; Tatenno et al., 2006; Tatenno, Zhang, & Nakano, 2008); from axial (Björk et al., 2002; Borgström et al., 2006; Jeppsson, Dick et al., 2008; Svensson et al., 2005; Panev, Persson, Skold, & Samuelson, 2003) to radial NW heterostructures (Ganjipour, Ek et al., 2012; Lin et al., 2003; Mohan, Motohisa, & Fukui, 2006; Noborisaka, Motohisa, Hara, & Fukui, 2005; Tilburg et al., 2010); and with metal catalyst (Duan et al., 2001; Nilsson et al., 2009; Shi et al., 2001; Vaddiraju et al., 2007;

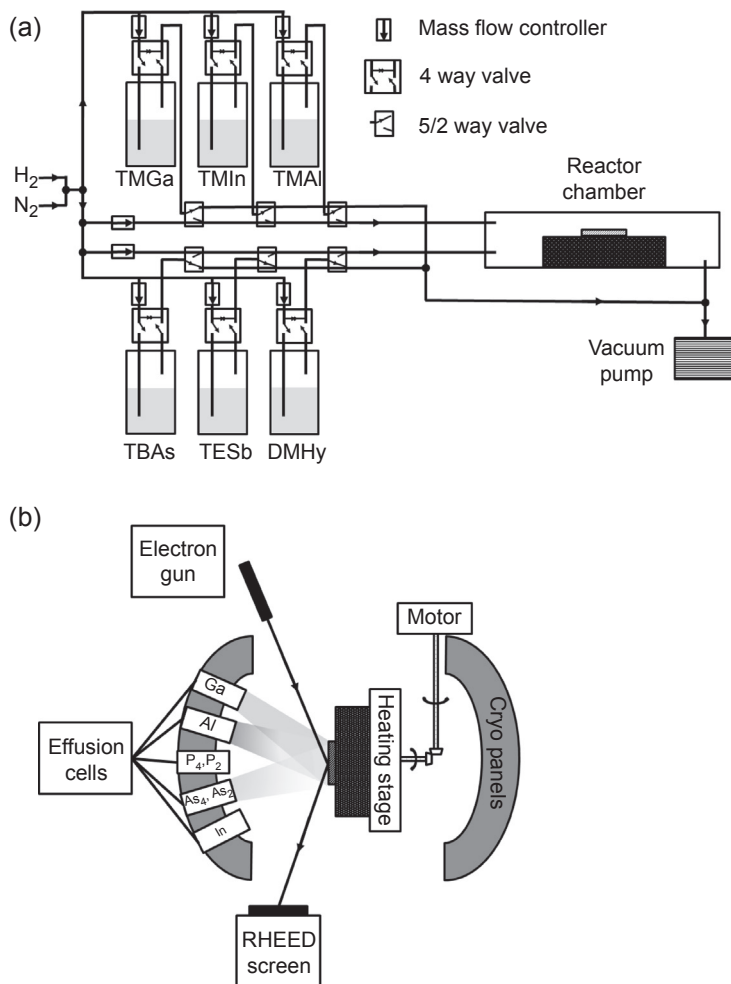


Figure 3.5 Scheme of (a) MOCVD A 5/2 way valve has 5 ports equally spaced and 2 flow positions. It can isolate and simultaneously bypass a passage way for the fluid which for example should retract or extend a double acting cylinder. A 4 way valve has four ports equally spaced round the valve chamber. The plug has two passages to connect adjacent ports. It can be used to isolate and to simultaneously bypass a sampling cylinder installed on a pressurized water line and (b) MBE setup.

Wu et al., 2003) and catalyst-free SA (Hamano et al., 1997; Motohisa, Noborisaka et al., 2004; Poole, Lefebvre, & Fraser, 2003) growth methods.

MBE is another growth method that allows the epitaxial growth of high-purity material and offers an abrupt interface between epi-layers in complex structures, promoting the development of device physics. It is a low-growth-rate technique based on the evaporation of solid (elemental) sources onto a heated substrate under ultra-high vacuum (UHV) conditions (Figure 3.5(b)). Because metal-assisted III–V NW growth is

very sensitive to the surface preparation (Fortuna & Li, 2010), an M source can be set up on the MBE to avoid contaminants from the M colloidal nanoparticle solution (Harmand et al., 2005). The high costs of precursors and system maintenance are the main drawbacks of this technique, responsible of the variation of process reproducibility. In addition, MBE is less versatile compared to MOCVD in terms of certain ternary and quaternary III-N materials growth due to the high vapor pressure of nitrides.

A hybrid technique combining features of MOCVD and MBE called chemical beam epitaxy (CBE) or metal organic MBE (MOMBE) was developed in the early 1980s (Veuhoff, Pletschen, Balk, & Lüth, 1981). In this case, the idea was to grow materials at UHV with metal-organic precursors. This system can use both solid and organometallic sources, but CBE also encountered similar issues as in MBE and MOCVD, the difficulty in growing nitride-based materials and the low throughput, hindering a widespread usage in the industry. Samuelson's group exploited III–V NW growth by CBE intensively on GaAs NWs (Persson, Larsson et al., 2004; Persson, Ohlsson et al., 2004), GaAs NW embedded with InAs quantum dots (Panev et al., 2003), and InAs NWs (Thelander et al., 2004). Growth of phosphide-based (Poole et al., 2003) and antimonide-based (Ercolani et al., 2009; Vogel, Boor et al., 2011; Vogel, De Boor et al., 2011) NWs was also reported.

3.2 Crystallographic properties

Progress in the bottom-up III–V NW synthesis has allowed the precise control of the crystalline structure, doping, heterostructure formation, and heteroepitaxial growth on Si, enabling the design of functional devices and their integration into a mainstream technology platform.

3.2.1 Crystallographic defects

Crystalline structure, as well as the occurrences of random structural defects and polytypism, can be precisely controlled during NW synthesis. While vacancy, anti-site, and interstitial defects are widely investigated in an III-N nanoscale system (Wang, Li, Gao, & Weber, 2010), twin boundaries (TBs) and SFs are usually considered in III–V nanostructures as main source of defects that can degrade device performance. For example, these defects can induce a variation of charge carrier concentration and an increment of phonon scattering (Schroer & Petta, 2010).

III–V NWs commonly exhibit a mixture of ZB cubic structure and wurtzite (WZ) hexagonal structure in the $\langle 111 \rangle$ direction (Algra et al., 2008; Caroff et al., 2008; Dayeh, 2010; Dayeh, Soci, Bao, & Wang, 2009; Dick, Caroff et al., 2010; Koguchi, Kakibayashi, Yazawa, Hiruma, & Katsuyama, 1992; Xiong, Wang, & Eklund, 2006), while their bulk counterparts usually crystallize in ZB. The ZB structure includes the stacking of monoatomic layers in the sequence of ...cAaBbCcA... in the $\langle 111 \rangle$ direction (Figure 3.6), whereas the WZ crystalline phase displays a stacking sequence of ...bAaBbA... in the $\langle 0001 \rangle$ direction. Due to the small difference in the cohesive energy of these two structures ($\Delta_{\text{ZB-WZ}} \leq 25$ meV) (Akiyama, Sano,

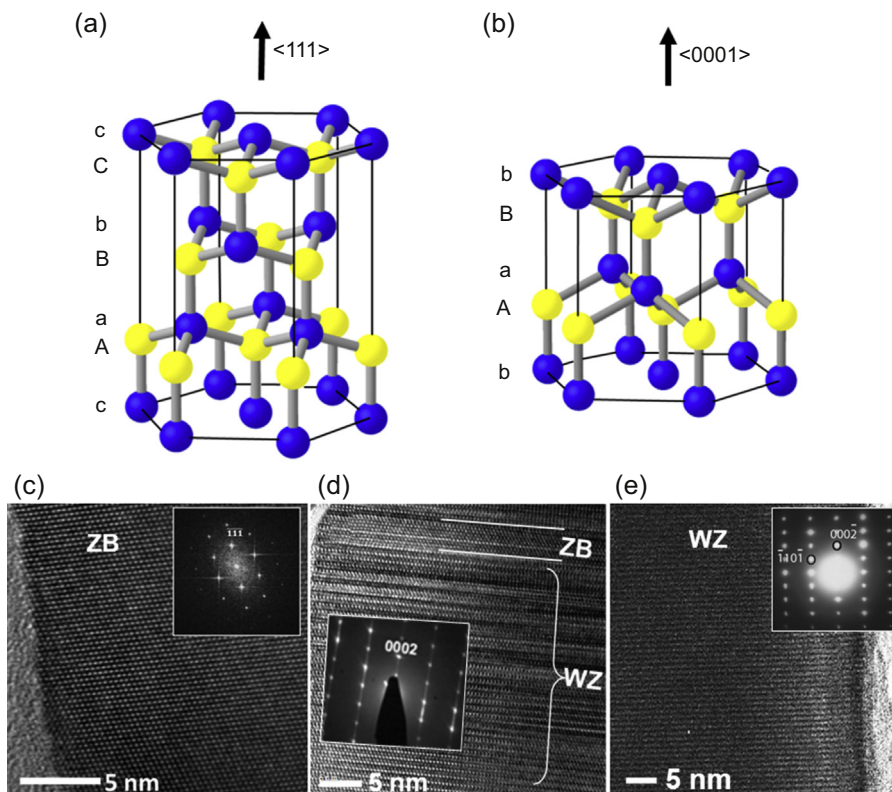


Figure 3.6 Polymorphism in III–V NWs. Ball-and-stick model of (a) the ZB structure in the $\langle 111 \rangle$ growth direction, showing the sequence of monoatomic stacking planes ...cAaBbCc... and (b) the WZ structure in the $\langle 0001 \rangle$ growth direction with stacking plane sequence ...bAaBb... (c–e) High resolution TEM images of (c) GaAs NW grown on GaAs (111)B surface. The electron diffraction pattern in the inset shows a pure ZB phase. (d) GaAs NW grown on Si (111) exhibiting a mixture of ZB and WZ phases. (Reprinted from Dayeh, Soci et al. (2009), with permission from Elsevier.) (e) SF free GaAs NW displaying pure WZ phase. (Reprinted with permission from Hoang et al. (2009). Copyright 2009, AIP Publishing LLC. Reproduced from Wilhelm et al. (2012), reproduced with permission of The Royal Society of Chemistry.)

Nakamura, & Ito, 2006; Glas, Harmand, & Patriarche, 2007), polytypism is observed by the appearance of small segments of ZB in WZ when an SF misplaces an “Aa” plane with a “Cc” plane, or small WZ segments appearing in ZB after the introduction of two sequential twin planes, or a twin plane between which the ZB segment rotates 60° around the $\langle 111 \rangle$ axis from the original ZB structure (Caroff, Bolinsson, & Johansson, 2011; Caroff et al., 2008; Tomioka, Motohisa, Hara, & Fukui, 2007). Other than these, a 20–40 nm long 4H polytype (...bAaBbCcBbA...) was observed right above the inserted ZB GaAsSb segment in the WZ GaAs NW (Dheeraj et al., 2008), and a six-monolayer superlattice consisted of twinned and ZB structure was

also reported as a new stacking sequence (...cAaBbCcBbAaCcA...) (Mariager et al., 2007). Dayeh et al. found that the gradual multiplication of SFs in the region between two edge defects were caused by edge-nucleated defects-induced steps at the liquid–solid interface, which is a distinctive defect multiplication mechanism in layer-by-layer NW growth (Dayeh et al., 2012).

In general, the defecting segments within the primary structure are nucleating at the triple-phase contact line on the small side facets or defects, acting as a form of stored surface and interface energy release (Johansson et al., 2006; Joyce et al., 2008). Notably, both the interface energies at the triple-phase boundary and the supersaturation of the liquid seed significantly affect the nucleation process and consequently determine the definitive crystallographic phase (Glas et al., 2007; Wilhelm, Larrue, Dai, Migas, & Soci, 2012). Therefore, the preferential growth of a particular phase can be controlled by tuning relevant VLS growth parameters such as the V/III ratio, the temperature, and the NW radius. It is generally accepted that high supersaturation (i.e., with high growth temperature, low V/III ratio, and small radii) promotes the appearance of a WZ crystalline phase (Dubrovskii & Sibirev, 2008; Dubrovskii, Sibirev, Harmand, & Glas, 2008; Glas et al., 2007; Glas, Patriarche, & Harmand, 2010). The fraction of WZ phases in InAs NWs was reported to increase with decreasing the growth temperature (Caroff et al., 2008; Johansson et al., 2010).

3.2.2 Doping

Controllable doping in III–V semiconductor NWs is critical in the broad range of applications, including electronics (Duan et al., 2001; Thelander et al., 2006), photonics (Yan et al., 2009), optoelectronics (Cirlin et al., 2009; Colombo, Heibeta, Gratzel, & Fontcuberta i Morral, 2009), and quantum transport devices (Riel et al., 2012; Tomioka & Fukui, 2011; Wallentin et al., 2010). To modulate the electrical (i.e., carrier concentration, band gap energy, mobility, etc.) and optical properties (i.e., absorption coefficient, dielectric constant, etc.) of NWs, it is of great importance to understand the dopant incorporation mechanism during the growth, and its influence on crystalline structure and composition characterization methods.

NW doping can be achieved by either *ex situ* or *in situ* doping methods. *Ex situ* doping methods include monolayer doping, where the surface covalently bonded dopant monolayers are annealed and diffused into the sample (Ho et al., 2009); gas-phase doping by annealing NW in the dopant ambient (Ford et al., 2010); solid-state diffusion through predeposition and drive in of spin-on-dopant (Ingole et al., 2008); and ion beam implantation, which allows doping concentrations beyond the equilibrium solubility limit (Borschel et al., 2011). On the other hand, the *in situ* doping can be done via the particle-seeded growth by the inclusion of dopant precursor, which mainly contains two mechanisms. The major one contains dopant incorporation from the liquid catalyst droplet to the NW core by VLS, as illustrated in Figure 3.7(a). The doping efficiency is limited by the dopant concentration in the liquid catalyst and the solubility in the solid III–V NW. Otherwise, dopants are incorporated from the sidewall in the vapor-phase-epitaxy (VPE) mode, consisting of dopant absorption, diffusion, and desorption as indicated by a dashed arrow in Figure 3.7(b)

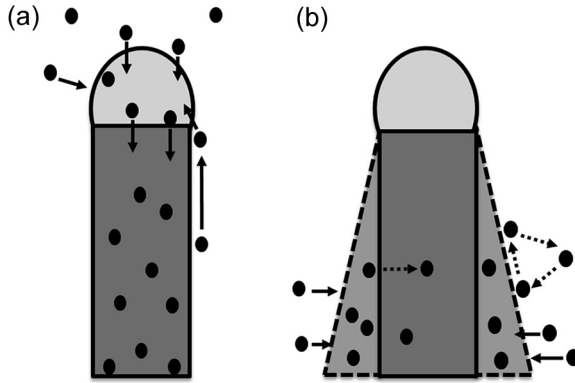


Figure 3.7 (a) Schematic diagram of dopant incorporation pathways via the VLS mode, where the dopants incorporate into the liquid catalyst, leading to a uniform doping concentration in the whole NW. (b) Schematic diagram of doping pathways via VPE mode comprising steps of dopants adsorption, migration, incorporation, and desorption on the sidewall of the NW.

(Casadei et al., 2013; Dufouleu et al., 2010; Schwalbach & Voorhees, 2009; Zhang, Tateno, Suzuki, Gotoh, & Sogawa, 2011).

Techniques such as hall measurement and secondary ion mass spectroscopy (SIMS) are widely used for determining the dopant incorporation and concentration in thin films. However, it is extremely challenging to adapt them into the characterization of an NW, high aspect ratio, one-dimensional system. Instead, some other methods are proposed to study the dopant distribution and *in situ* doping process.

Dopant concentration and carrier density are conventionally determined by electrical measurements, which includes resistivity mapping (Dheeraj et al., 2013; Dufouleu et al., 2010), field effect transistor (FET) characterization (Dayeh et al., 2007a; Rolland, Caroff, Coinon, Wallart, & Leturcq, 2013; Thelander et al., 2010; Zhang et al., 2011), and capacitance–voltage (CV) measurement (Roddaro et al., 2008). The difference and repeatability in doping concentration can be compared by a qualitative measurement of the resistivity between multicontacts or different NWs. On the other hand, a quantitative estimate of doping concentration and mobility can be extracted from the linear regime of the FET I – V characteristics. The free carrier concentration at flat-band conditions, usually referred to as the electrically active dopant concentration, $n = (\rho e \mu)^{-1}$, where $\rho = RS/l$ is the resistivity, R is the NW resistance, S is the cross-sectional area, l is the contact separation, and μ is the field-effect mobility. The latter can be evaluated by $\mu = g_m L^2 / C_g V_d$, where $g_m = (dI_d/dV_g)_{\max}$ is the transconductance, L is the channel length, C_g is the gate capacitance. For a circular cross-section, $C_g = 2\pi\epsilon\epsilon_0 L / \ln(2t_{ox}/r)$, and for hexagonal-shaped NW,

$$C_g = \alpha(2\pi\epsilon\epsilon_0 L) / \cos^{-1} \left(\left(t_{ox} + \frac{\sqrt{3}}{2} r^* \right) / r^* \right), \text{ with } r^* = 0.84r \text{ (Wunnicke, 2006).}$$

Using this method, Rolland et al. (Rolland et al., 2013) and Thelander et al. (Thelander et al., 2010) found that Si dopant primarily incorporated in the sidewall by radial overgrowth in case of Au-catalyzed InAs NWs grown in MBE and CBE, while

Zhang et al. (Zhang et al., 2011) demonstrated Si dopant to be predominantly incorporated in the core of the InAs wire through Au catalyst in MOCVD growth. The other method, CV characterization, allows quantifying the NW carrier concentration through an adapted radial metal-insulator-semiconductor FET (MISFET) model (Astromskas et al., 2010) and is more precise due to the direct measure of the gate capacitance without the use of assumptions relevant to parasitic capacitances and actual geometric gate capacitance.

Raman spectroscopy was reported to analyze the Si *in situ* doping mechanism, existence, concentration, and crystalline structure in the Ga-catalyzed GaAs NW grown by MBE (Dufouleur et al., 2010; Ketterer, Uccelli, & Morral, 2012). Si and Ge are amphoteric in III–Vs, which could result in either n-type or p-type doping and can be distinguished using Raman spectroscopy. The transverse optical (TO) and longitudinal (LO) phonon modes of GaAs can be identified at wavenumbers 263 and 288 per centimeter, while the lower density peaks at 384 and 393 per centimeter are attributed to local vibrational mode (LVM) of Si atoms on Ga sites (n-type) and As (p-type) sites, respectively. The position of LVM mode at 393 per centimeter and the increasing LVM to modes ratio from the tip to the base along the NW revealed a p-type behavior with higher doping concentration at the base of the GaAs NW, implying the possibility of dopant incorporation through the side facets.

Sophisticated tools like the atom probe tomography (APT) (Müller, Panitz, & McLane, 1968) performed on a local electrode atom probe (LEAP) microscope can be used to do the 3D atomic-resolution composition mapping of an NW from the sequential field evaporation of individual ions from the NW tip. Lauhon's group mapped the position of single Au atoms in an MOCVD grown InAs NW and found the interface between the $\text{Au}_{0.9}\text{In}_{0.1}$ catalyst and the InAs NW is extremely abrupt (less than 0.5 nm) (Perea et al., 2006). Sequentially, Du et al. demonstrated the elemental mapping of an Si-doped GaAs NW, where the distribution of Si dopants, carbon, hydrogen, and oxygen contaminations were measured and reconstructed into a 3D graph (Du et al., 2013).

Scanning tunneling microscopy (STM) is an alternative technique, being able to detect the quantitative information down to atomic precision (e.g., facet morphology, atomic structure, and surface composition characterization) (Bolinsson et al., 2009; Mikkelsen, Skold et al., 2004; Xu et al., 2012). It has been used to detect the composition and diffusion of Sb in InAs/InAs_{1-x}Sb_x NW (Xu et al., 2012) and Mn in Ga_{1-x}Mn_xAs/GaAs superlattices (Mikkelsen, Ouattara et al., 2004).

In the meantime, other techniques such as out-of-plane X-ray diffraction and imaging (Davydok et al., 2013), X-ray energy-dispersive spectroscopy (XEDS) (Xu et al., 2012; Yang et al., 2013), electron energy loss spectroscopy (EELS) (Yang et al., 2013), and photoemission electron microscopy (Hjort et al., 2011) are also used to identify and map dopant incorporation in NWs.

3.2.3 Homo- and heterojunction formation

Compared to other nanostructure topologies, NWs have a unique degree of freedom to design nanoscale homo-/heterojunctions or to form monolithic junctions. Numerous physical phenomena arising from such low-dimensional nanostructures with large

surface-to volume ratio could be explored in terms of carrier confinement, band structure, oscillator strength, spin-orbit interaction, etc.

NW homojunctions, including p-n radial/axial homojunction and controlled coherent polytypism in a single III–V NW, are elaborated following the VLS mechanism. The typical growth process of a radial or axial homojunction relies on the switching of the dopant precursors following a three-step procedure. The first dopant precursor is switched off after the growth of the first NW section following by its evacuation from the growth reactor under continuous flow of III–V organometallic precursors; then the second doping reactants starts to be injected in the chamber reactor to dope the subsequent section. When all the precursors are incorporated into the liquid catalyst, even during the dopant switching, the crystalline growth in the longitudinal direction will be favored, forming an axial homojunction (Figure 3.9(a)). An axial p-n/p-i-n homojunction provides a well-defined active region, allowing the tunable injection of electrons and holes without any light-screening phenomena (Goto et al., 2009; Lysov et al., 2011; Minot et al., 2007). On the other hand, when the second doping reactant is dissociated and absorbed at the surface of the NW, a radial homojunction is formed with an epitaxial process similar to planar growth of thin films (Figure 3.9(b)). Particular attention has been paid to radial p-i-n or p-n homostructure growths for their superior carrier collection efficiency under light illumination, where light absorption direction is orthogonal to the carrier collection (Colombo et al., 2009).

III–V NWs have potential to create an original homojunction based solely on the crystalline structure difference, i.e., ZB and WZ. This feature is totally new and specific to III–V NW synthesis, since only one crystalline structure (the cubic ZB structure) is thermodynamically stable for III–V materials. Twin-plane superlattices based on the repetition of ZB segments with constant distance between twin planes (Algra et al., 2008; Algra et al., 2011; Caroff et al., 2008) (Figure 3.8(b)) and highly reproducible polytypism with alternative WZ and ZB segments (Caroff et al., 2008; Dick, Thelander, Samuelson, & Caroff, 2010; Figure 3.8(c)) within a single III–V NW have been successfully reported, leading to advanced optical studies originated from the crystallographic inhomogeneity. In particular, twinning superlattices growth has been observed for InAs (Caroff et al., 2008), InP (Algra et al., 2008; Shen, Bando, Liu, Tang, & Golberg, 2006), and GaP (Algra et al., 2011, 2010; Xiong et al., 2006) NWs. A model based on the influence of the liquid catalyst distortion on the growth process has been proposed to explain the twinning superlattice growth mechanism as shown in Figure 3.8(a) (Algra et al., 2008; Johansson et al., 2006). NWs grow in a layer-by-layer scheme with the nucleation point located at the triple line edge. The energy for nucleus formation relies on both the liquid–solid contact angle and the tilt angle of the external facet. The polar side facets with the orientation of $\{111\}A$ and $\{111\}B$ are expanding or shrinking individually during the growth because they are tilted from the $\langle 111 \rangle$ vertical direction, resulting in the transition of the NW cross-section shape from hexagonal to a triangle-like shape. As a result, the side facets may change to the alternative orientation and twin planes are formed in order to relax the strain (Algra et al., 2008; Algra et al., 2011; Johansson et al., 2006; Karlsson et al., 2007), after which the triangle-like shape cross-section evolves into the hexagonal shape and the cycle starts repeating. The twinning superlattices are naturally occurring

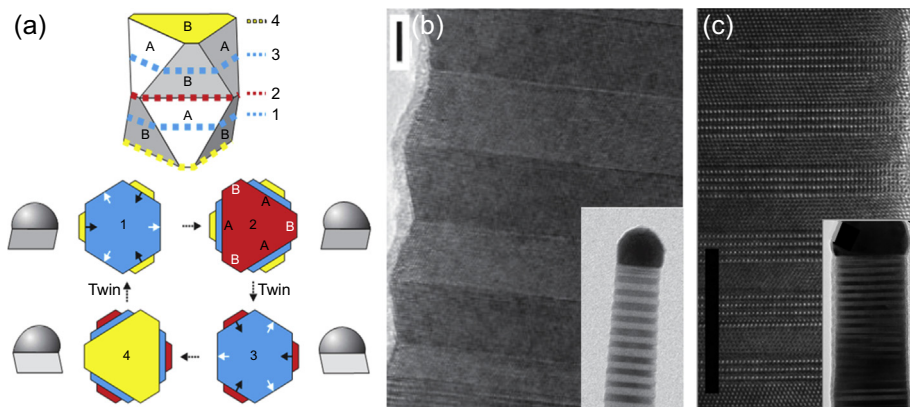


Figure 3.8 (a) Model for periodic twinning evolution in an NW showing ZB structure with nonparallel side facets. (b) TEM images of InP NW twinning superlattice with a diameter of 50 nm. Scale bar: 5 nm. (Adapted with permission from Macmillan Publishers Ltd: Nature [Algra et al. \(2008\)](#). Copyright 2008.) (c) TEM images of InAs NW superlattices with periods of alternating ZB and WZ structure (each 8 bilayers thick). Scale bar: 10 nm. (Adapted with permission from [Dick, Thelander, et al. \(2010\)](#). Copyright 2010, American Chemical Society.)

at specific growth temperatures and NW diameters (the larger the diameter, the longer the spacing between twin planes) ([Caroff et al., 2008](#)). Meanwhile, dopants, such as Zn ([Algra et al., 2008, 2011](#)), can also help to reduce the activation barrier for two-dimensional nucleation growth of ZB segment and to produce long-range ordered twinning superlattices. In this case, the spacing between twin planes is proportional to the Zn doping concentration together with the NW diameter.

NW heterojunctions also provide diversity and flexibility in the design of nanostructure and allow more complex and advanced functionalities during the bottom-up growth. A heterostructure is the combination of different materials with diverse properties. The synthesis of quasi-1D structures opens up opportunities for heterointegration compared to a thin-film counterpart. The small diameter gives NWs the inherent ability to efficiently relieve the lattice mismatch-induced strain through lateral relaxation ([Bao et al., 2008](#)). Axial and superlattice heterostructures are formed when new or alternative reactants are incorporated into the liquid alloy, resulting in longitudinal elongation, as illustrated in [Figure 3.9\(c\) and \(d\)](#). Otherwise, if the new reactants are absorbed at the NW surface, a shell will grow on the original NW surface, promoting the formation of a core-shell NW ([Figure 3.9\(e\)](#)). Changing reactants in the radial growth regime will result in the formation of a core-multi-shell geometry ([Figure 3.9\(f\)](#)). The precise control of the III–V heterostructure growth conditions enables the fabrication of custom-built NW architectures. For instance, GaAs/Al_xGa_{1-x}As radial Type I heterostructures ([Fontcuberta I Morral, Spirkoska et al., 2008; Gallo et al., 2011; Heigoldt et al., 2009; Heiss et al., 2013; Sladek et al., 2010; Spirkoska, Abstreiter, & Morral, 2009](#)) are promising in the applications of high electron mobility transistors (HEMTs), photo-detector, and solar cells, where both electrons and holes tend to be localized in the lower

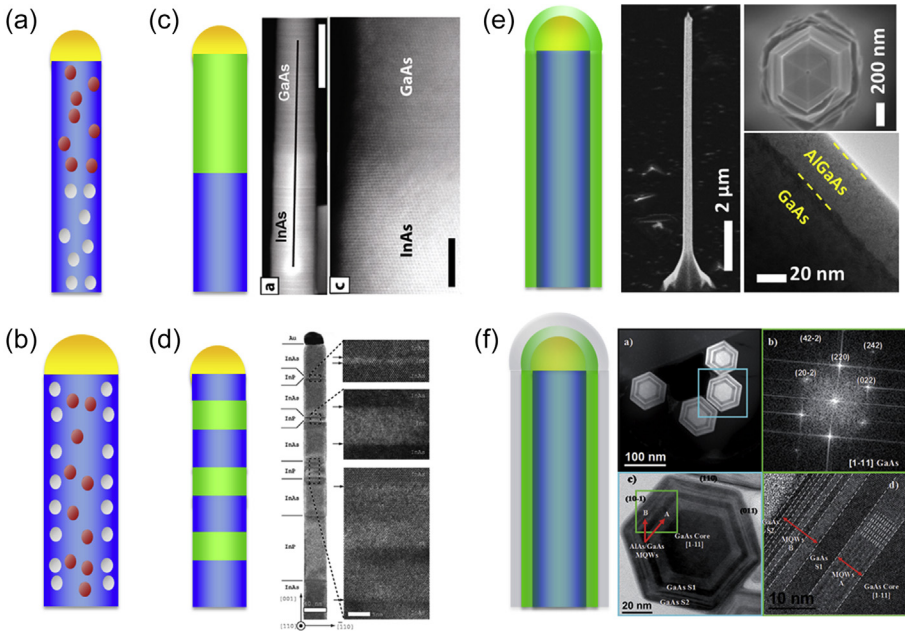


Figure 3.9 NW homojunctions and heterostructures. Axial and radial p-n homojunctions showing in (a) and (b). (c) An axial NW heterostructure with the TEM image showing an InAs-GaAs junction. (Adapted with permission from [Dick, Bolinsson, Borg, and Johansson \(2012\)](#). Copyright 2012, American Chemical Society.) (d) An NW with axial alternating materials. TEM image displaying an InAs NW containing four sequential InP barriers. (Reprinted with permission from [Björk et al. \(2002a\)](#). Copyright 2002, AIP Publishing LLC.) (e) A radial (core/shell) NW heterostructure. SEM image presenting an as-grown GaAs/AlGaAs NW and the TEM image showing a clear boundary. (f) Schematic of core-multishell NW. High angular annular dark field (HAADF) image showing cross-sections of multiple quantum well NWs, consisting of multiple alternative AlAs and GaAs shells on an AlAs core. (Adapted with permission from [Heigoldt et al. \(2009\)](#). Copyright 2009, Royal Society of Chemistry.)

bandgap material (GaAs). Alternatively, Type II staggered band alignment, e.g., GaAs/InAs ([Messing et al., 2011](#); [Ohlsson et al., 2002](#); [Panev et al., 2003](#)), formed by periodically distributed band-edge alignment, should provide better performances for photodetectors since electrons and holes could be dragged into opposite directions, hence decreasing the probability of electron–hole recombination. The uncommon broken gap type III heterostructure GaSb(p)/InAs(n) NW leads to efficient band-to-band tunneling and to possible higher current densities ([Borg et al., 2012](#)).

Recently, intersected or branched nanowires have gained paramount interests thanks to their capability of realizing interconnection during growth and offering a promising platform for low-dimensional fundamental condensed-matter physics research ([Alicea, Oreg, Refael, Oppen, & Fisher, 2011](#); [Sau, Clarke, & Tewari, 2011](#)). Self-assembly of monolithic junctions ([Dai et al., 2011](#); [Dalacu, Kam, Austing, & Poole, 2013](#); [Kang et al., 2013](#); [Plissard et al., 2013](#)) and two-step catalytically

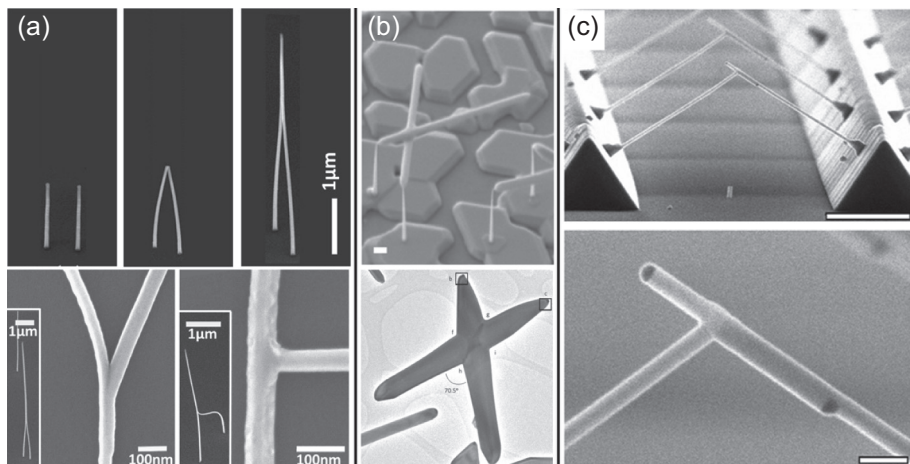


Figure 3.10 (a) Evolution of monolithic GaAs junction formation. (Reprinted with permission from Dai et al. (2011). Copyright (2011) American Chemical Society.) (b) InSb nanocrosses forming through the merging process between two InSb NWs grown on InP/InAs stems. (Adapted by permission from Macmillan Publishers Ltd: Nature Nanotechnology (Plissard et al. (2013). Copyright 2013.) (c) SEM image of a pair of connected NWs grown on InP ridges pitched at 3.5 μm . The scale bar is 1 μm . Close-up of the intersection. The scale bar is 100 nm. (Reprinted with permission from Dalacu et al. (2013). Copyright (2013) American Chemical Society.)

branched NW growth has become controllable (Dick et al., 2004; Jiang et al., 2011; Suyatin et al., 2008). Dai et al. demonstrated that self-assembly of monolithic GaAs NW junctions can be achieved by simultaneously tuning the diameter, the height, and the interdistance between two NWs to the point where the electrostatic energy between polar surfaces exceeds the mechanical energy required to bend the NWs to the point of contact (Figure 3.10(a); Dai et al., 2011).

Lately, Plissard et al. discussed the ability of horizontal InSb NWs grown from InP/InAs stems to meet and merge into T or X junctions under specific conditions (Figure 3.10(b)) and their potential for the exchange of Majorana fermions in quantum transport study (Plissard et al., 2013). Dalacu et al. reported their unique control of interconnected InAs NWs grown on InP ridge templates through selective-area growth (Figure 3.10(c)), which open up new opportunities for large-scale functional device integration (Dalacu et al., 2013).

4.2.4 Heteroepitaxial growth

The growing demand for the implementation of high-performance III–V structures into the well-established and functional silicon platform is facing technological challenges due to lattice mismatch, thermal expansion coefficient difference, and polar/nonpolar surface nature. However, the quasi 1D geometry characteristics of the NW, i.e., the large surface-to volume ratio and small diameter, promote the strain relaxation coming from lattice mismatch, thus reducing the lattice-matching

requirement existing in conventional thin-film growth, and enabling direct high-quality heteroepitaxy without introducing a buffer layer. A non-exhaustive list of lattice mismatches of III–V on non III–V is reported, e.g., GaAs (4.1%) (Bao et al., 2008; Dick, Deppert, Samuelson, Wallenberg, & Ross, 2008; Fauzia, Vincenzo, Silvia, & Faustino, 2008; Huang et al., 2010; Ihn, Ryu, & Song, 2010; Jung-Hyun et al., 2010; Kang et al., 2010; Khorenko et al., 2004; Mårtensson et al., 2004; Plissard, Larrieu, Wallart, & Caroff, 2011; Soo-Ghang, Jong-In, Young-Hun, Yong Lee, & Il-Ho, 2007; Tomioka, Motohisa, Hara, Hiruma, & Fukui, 2010), InAs (11.6%) (Chuang et al., 2007; Dayeh, Yu, & Wang, 2007c; Koblmüller et al., 2010; Mandl et al., 2006; Pratyush Das et al., 2013; Roest et al., 2006; Soo-Ghang & Jong-In, 2007; Tomioka, Motohisa, Hara, & Fukui, 2008; Wei et al., 2009), InP (8.1%) (Boles, Thompson, & Fitzgerald, 2009; Chuang et al., 2007; Dalacu et al., 2009; Mårtensson et al., 2004; Roest et al., 2006), GaP (0.37%) (Boulanger & Lapierre, 2012; Dick et al., 2008; Mårtensson et al., 2004; Roest et al., 2006), and ternary-alloy (Mattila, Hakkarainen, Lipsanen, Jiang, & Kauppinen, 2006; Mattila, Hakkarainen, Mulot, & Lipsanen, 2006; Moewe, Chuang, Crankshaw, Chase, & Chang-Hasnain, 2008; Mohseni, Maunders, Botton, & Lapierre, 2007; Ng et al., 2012; Plissard, Dick, Wallart, & Caroff, 2010; Shin et al., 2013; Svensson et al., 2008; Tomioka et al., 2010 on Si; InP on Ge (3.7%) (Bakkers et al., 2004); and even GaAs and InAs on graphite (Hong, Lee, Wu, Ruoff, & Fukui, 2012; Munshi et al., 2012). III–V NW-based devices integrated on Si, such as photodetectors (Bao et al., 2008), photovoltaics (Bao et al., 2008; Shin et al., 2013), LEDs (Svensson et al., 2008; Tomioka et al., 2010), tunneling diodes (Bessire et al., 2011), and surrounding-gate FETs (Rehnstedt, Martensson, Thelander, Samuelson, & Wernersson, 2008; Tanaka et al., 2010), have been demonstrated relying on the successful III–V/Si heteroepitaxial growth.

As discussed in Section 3.1.1, III–V NWs preferably grow on (111)B substrate in the $\langle 111 \rangle$ direction. However, due to the unpolarized surface of the Si (111) substrate, they tend to grow in the four equivalent $\langle 111 \rangle$ directions with one perpendicular to the Si substrate and three other orientations having a 19.5° angle with respect to the surface and 120° between in-plane projections of one another (Figure 3.2(a) and (b)). With the proper substrate preparation (buffer oxide etchant was used for native oxide removal) and under specific growth conditions, Wei et al. were among the first who demonstrated the growth of extremely high-density vertical Au-catalyzed GaAs and InAs NWs (Figure 3.11(a)) on Si (111) substrate, suitable for large-scale application in photovoltaics and photodetectors (Bao et al., 2008; Wei et al., 2009). To be more specific, Si^{1+} , Si^{2+} and Si^{3+} structures are usually observed on the Si (111) surface (Hattori et al., 1996; Himpfel, Mcfeely, Taleb-Ibrahimi, Yarmoff, & Hollinger, 1988). Tomioka et al. reported that InAs NWs could grow vertically on the Si (111) surface presenting only As-incorporated Si^{3+} and In-terminated Si^{1+} properties (Figure 3.11(b)), which was reconstructed under proper precursor flow and growth temperature (Tomioka et al., 2008). Recently, remarkable advances in the uniform catalyst-free growth of high-density vertical $\text{InAs}_y\text{P}_{1-y}$ NWs on an entire 2-inch Si (111) substrate have also allowed the feasibility of a heterojunction solar cell of n-type $\text{InAs}_y\text{P}_{1-y}$ and p-type Si at wafer-scale, making it compatible with industrial fabrication standards (Shin et al., 2013).

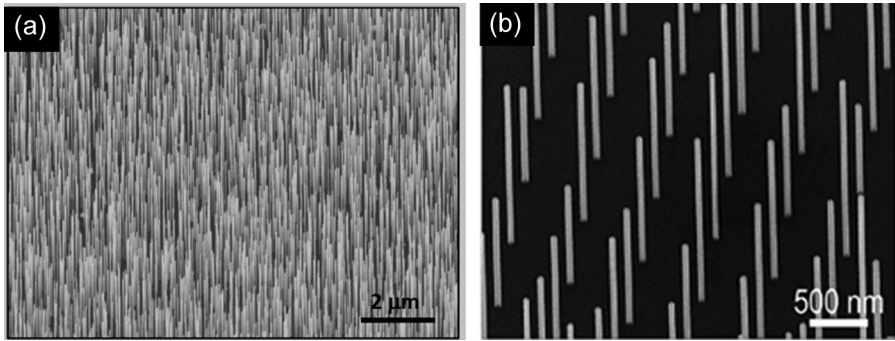


Figure 3.11 (a) 45° tilted SEM image of Au-catalyzed InAs NWs grown vertically on Si (111) substrate. (b) 45°-tilted view of InAs NW array on patterned Si substrate without catalyst. (Reprinted with permission from Tomioka et al. (2008). Copyright (2008) American Chemical Society.)

Toward the integration of high-performance III–V NW-based devices with the mature Si-based technology, it is highly desirable to be able to manage the positioning of vertical NWs during the growth. Two approaches are commonly used. The first relies on patterned arrays of metal seeds (mainly Au), serving as growth catalysts for VLS growth. However, the use of Au catalyst for III–V NWs on Si substrate was reported to have a detrimental effect on the growth, e.g., migration and oxidation of Si on Au prior to growth (Boulanger & Lapierre, 2012; Roest et al., 2006); and on some properties, e.g., Au incorporation in NW introducing deep-level traps. The second can use SA growth without introducing an exterior catalyst on an Si substrate covered by a thin SiO₂ layer with small openings. Notably, Plissard et al. reported a high-yield growth of Ga-catalyzed GaAs NW arrays on Si, demonstrating that Ga droplets formed *in situ* before the NW growth on the pre-patterned oxide-free SiO₂ openings could efficiently replace the standard Au catalyst (Plissard et al., 2011). Moreover, through Si surface engineering, III–V NWs can be selectively grown on Si even without any catalysts (Tomioka, Tanaka, Hara, Hiruma, & Fukui, 2011; Wei et al., 2009).

During the heteroepitaxial growth, misfit dislocations are usually introduced at the interface between two lattice-mismatch materials, which could be reduced by decreasing the NW diameter. Calculations explain that the strain is shared by the NW and the substrate, and mainly relaxed along the lateral direction. A critical radius exists below which coherent growth occurs without interfacial dislocation (Ertekin, Greaney, Chrzan, & Sands, 2005; Glas, 2006). A defect-free coherent growth of GaAs NW on Si with 27 nm in diameter was demonstrated in Figure 3.12(a) and (b) (Katsuhiko, Yasunori, Junichi, Shinjiroh, & Takashi, 2009). For larger-diameter NWs, Ng et al. illustrated the evolution of a defective region at the interface between InGaAs/GaAs NW and Si with increasing diameter size of 50, 120, and 740 nm. The thinner the NW, the fewer the dislocations, and shorter defective region length was observed, as shown in Figure 3.12(d–h) (Ng et al., 2012). A defective region length of 3.5 nm was observed in the NW of 50 nm in diameter at the interface

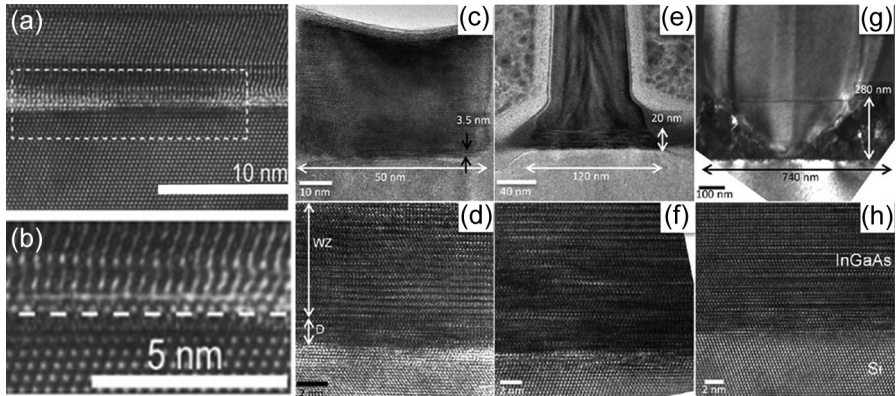


Figure 3.12 (a) Cross-sectional TEM image of a GaAs NW of 27 nm in diameter grown on Si(111). (b) The magnified image of the dashed rectangle shown in (a), showing the defect-free heterointerface of GaAs and Si(111) with 4.1% lattice mismatch. (Copyright IOP Publishing. Reproduced with permission from [Katsuhiko et al. \(2009\)](#). All rights reserved.) (c), (e), (g). TEM images of InGaAs/GaAs core–shell nanopillar with base diameters of 50, 120, and 740 nm, with the zoom-in images presented in d, f, h, respectively. The thickness of interface defective region increases from (d) 3.4 to (h) 280 nm, relaxing the 6% misfit stress between InGaAs and Si. (Reprinted with permission from [Ng et al. \(2012\)](#). Copyright (2012) American Chemical Society.)

([Figure 3.12\(d\)](#)), while a 280 nm defective region was displayed in NW with a diameter of 740 nm ([Figure 3.12\(h\)](#)).

The progress in the control of growth direction and the optimization of interface quality in the heteroepitaxial growth of III–V NWs on Si open up more opportunities in high-performance electronic and photonic applications.

3.3 Applications of III–V nanowires

Thanks to their small dimension and quasi 1D characteristics, NWs are highly considered as optoelectronic components and emerging research devices beyond CMOS by the International Technology Roadmap for Semiconductors. Among them, III–V NWs are particularly suited for the applications of FETs, photodetectors, and miniature light sources, thanks to their high electron mobility, direct bandgap, and feasibility in bandgap engineering.

3.3.1 Electronics

Silicon transistors have reduced in size by over a million times following Moore's law since their invention in the late 1940s. Their operation speed increased by over a billion times thanks to excellent process control and recent advancements in strain engineering ([Welser, Hoyt, Takagi, & Gibbons, 1994](#)) metal gate stack and high-k dielectrics ([Wilk, Wallace, & Anthony, 2001](#)) and transistor architecture ([Hisamoto](#)

et al., 2000). However, it is expected that downscaling of the current planar Si-based technology will eventually reach its physical limits below 10 nm technology node. Among various materials and structures being investigated, III–V NW field-effect transistors (NWFETs) are considered as promising candidates on the roadmap for scaling down of electronic devices thanks to their intrinsic properties of high electron mobility and good interface quality with high- k gate dielectric. Moreover, NWs offer more degrees of freedom for the 3D integration scheme with a full control of the potential of the conducting channel. With an omega-shaped gate or gate-all-around (GAA) configuration, NWFETs offer better electrostatic control in terms of on/off current ratio, transconductance, and short channel effects compared to conventional planar transistors. Fabrication and performance of III–V NWFETs of horizontally dispersed NWs, planar as-grown NWs, and vertical NW arrays with surrounding gate will be discussed.

Intensive investigations have been carried out on lateral NWFETs where III–V NWs are successively removed from their initial grown substrate and transferred on a prepatterned SiO_2/Si substrate for future lithography process. Source and drain electrodes are then defined, followed by the global back-gate metallization (Dayeh, Aplin et al., 2007; Dayeh, Susac, Kavanagh, Yu, & Wang, 2009; Ford et al., 2010; Thelander, Caroff, Plissard, Dey, & Dick, 2011; Yang et al., 2013) or high- k material deposition and omega shape top-gate patterning (Dayeh, Aplin et al., 2007; Dey et al., 2012; Lind, Persson, Samuelson, & Wernersson, 2006; Storm, Nylund, Borgstrom et al., 2011). Progress on InAs (Dayeh, Aplin, et al., 2007; Dey et al., 2012; Ford et al., 2010; Storm, Nylund, Samuelson, & Micolich, 2011; Thelander et al., 2011), GaAs (Schricker, Davidson, Wiacek, & Korgel, 2006), InP (Storm, Nylund, Borgstrom et al., 2011), InSb (Yang et al., 2013), InAs/InP (Jiang et al., 2007), and InAs/InAsP (Lind et al., 2006) dispersed NW FETs has been thoroughly reported in the literature. Among the numerous choice of III–V materials, InAs is particularly attractive due to its high mobility at room temperature and inherent surface Fermi-level pinning in the conduction band, which allows formation of n-type ohmic contacts. Dayeh et al. performed a systematic study on InAs NWFET regarding impact of surface states (Dayeh, Soci, Yu, Yu, & Wang, 2007a, 2007b), carrier mobility (Dayeh, Aplin, et al., 2007), field-dependent transport (Dayeh, Susac, Kavanagh, Yu, & Wang, 2008), diameter dependence (Dayeh, Yu, & Wang, 2009), and influence of the crystal structure (Dayeh, Susac et al., 2009). Transfer curve hysteresis is normally observed in NW FETs due to the surface states. By reducing the gate voltage sweep rate, trapping and detrapping charge mechanism can be controlled, resulting in a reduced hysteresis. As a result, to extract the intrinsic NW transport parameters, one needs to ensure the NW surface is charge neutralized or passivated. At slow and fast sweep rate, electron mobility of $\sim 16,000 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $\sim 6580 \text{ cm}^2/(\text{V}\cdot\text{s})$ are extracted, respectively, demonstrating that the slower the sweeping rate, the higher measured transconductance. Furthermore, the transconductance and the mobility are degraded at both vertical and lateral high electric field due to the enhanced phonon scattering coming from heating effects and possible morphological degradation. Lower mobility and higher average carrier concentration are observed in smaller diameter NWs caused by the presence of an electron surface accumulation layer that

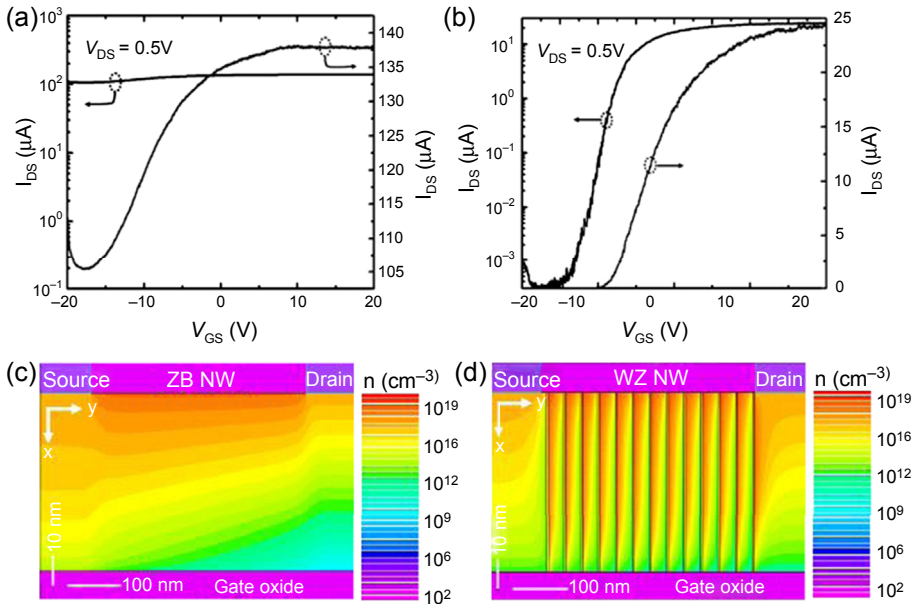


Figure 3.13 Transfer characteristics of long-channel (LSD = 3.4 μm) back-gate InAs NWFETs made from (a) pure ZB ($D_{\text{NW}} \sim 81$ nm) showing $I_{\text{on}}/I_{\text{off}} < 2$ and (b) WZ/ZB ($D_{\text{NW}} \sim 60$ nm) InAs NWs showing $I_{\text{on}}/I_{\text{off}} > 104$ at $V_{\text{DS}} = 0.5$ V. The corresponding 2D simulation in (c) and (d) showing contour plots of carrier concentration extracted at $V_{\text{DS}} = 0.5$ V and $V_{\text{GS}} = -20$ V in an InAs slab, with stronger depletion penetrating deeper across the channel body in (d). (Reprinted with permission from Dayeh, Susac et al. (2009). Copyright (2009) WILEY-VCH.)

increases the surface scattering, while higher mobility and lower average carrier concentration are expected for larger-diameter NWs due to bulk-like transport property. It is also essential to understand the correlation between the crystal phase and the electronic transport behavior, since polytypism is typically observed in III–V NWs. WZ InAs NWs with numerous SFs exhibited improvement of the on/off ratio compared to pure ZB NWs, but lower current level (Figure 3.13(a) and (b)), which was also observed by Thelander et al., where NWs with mixture of two phases presented a higher resistivity by two orders of magnitude compared to single-phase NWs (Thelander et al., 2011). The nonzero spontaneous polarization charges present at the WZ/ZB interfaces suppress carrier accumulation at the NW surface, resulting in a full depletion of the channel (Figure 3.13(d)). These results pave the way for incorporating III–V NWs into future electronic devices. With the advances in the synthesis of III–V, Li et al. achieved the self-assembly of planar $\langle 110 \rangle$ GaAs NWs on semi-insulating GaAs (100) substrate (Fortuna & Li, 2009), where GaAs NWs were capped with an AlGaAs shell (Miao & Li, 2011). Excellent transistor properties were demonstrated on such single GaAs FETs with subthreshold slopes as low as 150 mV/dec, and mobility of ~ 4100 $\text{cm}^2/(\text{V} \cdot \text{s})$.

On the other hand, vertical III–V NWFETs on III–V substrate (Bryllert, Wernersson, Froberg, & Samuelson, 2006; Thelander, Frobergfroberg, Rehnstedt, Samuelson,

& Wernersson, 2008) or on Si substrate (Rehnstedt et al., 2008; Tanaka et al., 2010; Tomioka, Yoshimura, & Fukui, 2012a, 2011) with a wrap-gate topology further improve the gate controllability and efficiently suppressed short-channel effect. An InAs vertical NWFET on InAs substrate through 3D device fabrication process was first reported in 2005 (Bryllert, Samuelson, Jensen, & Wernersson, 2005), which opened new schemes for future heteroepitaxial integration of SA-grown InAs (Bryllert et al., 2006; Rehnstedt et al., 2008; Tanaka et al., 2010; Thelander et al., 2008) (Figure 3.14(a–c)) and InGaAs (Tomioka et al., 2012a; Tomioka, Yoshimura et al., 2011) NWFET on an Si platform. Advanced optimization on the design of the NW architecture was introduced by Tomioka et al., where a complexed InGaAs/InP/InAlAs/InGaAs core-multishell structure (Tomioka et al., 2012a; Tomioka, Yoshimura et al., 2011) exhibited improved intrinsic characteristics, i.e., a higher drain current, a steep subthreshold slope (75 mV/dec), and a low drain-induced barrier lowering (35 mV/V) thanks to the shell passivation and the formation of an electron gas inside the InGaAs channel (Figure 3.14(d–f)).

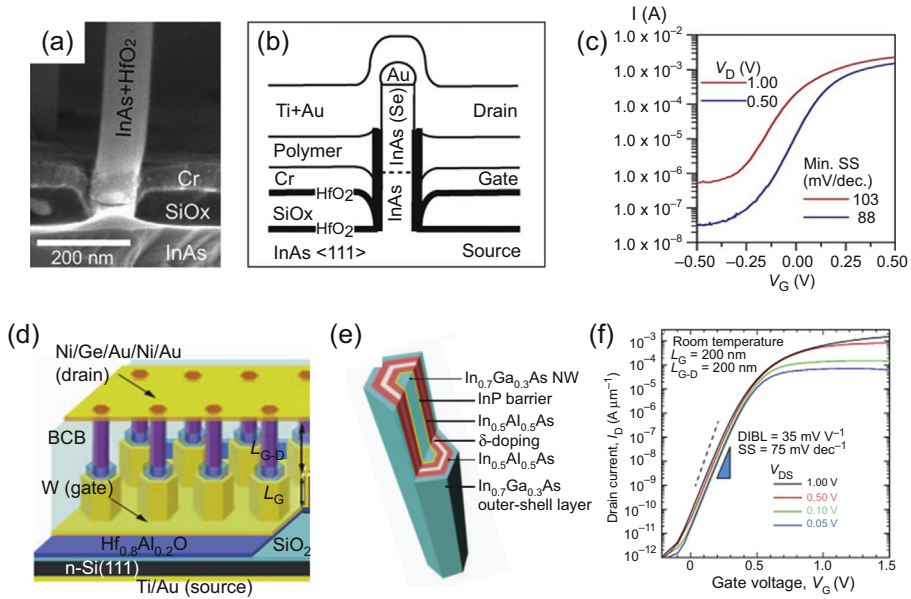


Figure 3.14 (a) Side view of a cleaved vertical InAs NWFET on InAs showing an SiO_x layer lifts the gate pad from the InAs source contact as schematized in (b), with the transfer characteristics of the device with $L_G = 50$ nm at the voltage of $V_D = 0.5$ (bottom) and 1.0 V (top) presented in (c). (Reprinted with permission from Thelander et al. (2008). Copyright 2008, IEEE.) (d) Structure of surrounding gate transistor with InGaAs/InP/InAlAs/InGaAs NWs connected in parallel with the drain metal on Si. The NW consists of InGaAs NW core wrapped with InP/InAlAs/ δ -doped InAlAs/InAlAs/InGaAs multilayers as illustrated in (e). (f) Transfer performance of this device with $L_G = 200$ nm and $L_{G-D} = 50$ nm showing low subthreshold slope (SS) and drain-induced barrier lowering (DIBL).

(Adapted with permission from Macmillan Publishers Ltd: Nature (Tomioka et al. (2012a). Copyright 2012.)

3.3.2 Photonics

Among the great features of NWs, bandgap engineering of III–V alloys offers great promise for photonic applications over a wide spectral range (Hyun et al., 2013; Mi, 2009).

The 1D morphology of NWs gives them the ability to guide light, similar to optical fibers. Moreover, III–V NWs can be pushed to subwavelength diameters and exhibit better light guidance thanks to their high refractive index with respect to the surrounding environment (Hua, Motohisa, Ding, Hara, & Fukui, 2007; Maslov & Ning, 2004). The finite length of the NW intrinsically generates Fabry–Pérot resonances due to the reflection on its end-facets (Ning, 2010). However, the rather poor quality factor obtained using as-grown end-facets (Hua et al., 2007; Maslov & Ning, 2003; Yang et al., 2009) has led to resonance improvement alternatives, such as using Bragg (Chen & Towe, 2006; Zhang & Loncar, 2008) or metallic mirrors (Friedler et al., 2008, 2009). Single GaSb NW near-infrared lasers have been demonstrated for telecommunications applications (Chin et al., 2006), as has stimulated emission in InGaAs/GaAs core–shell nanopillar grown on Si (Chen et al., 2011), originated from its diameter that is larger than effective wavelength and that supports whispering gallery modes. Thanks to surface passivation offered by shell growth, lasing was observed in GaAs/GaAsP core–shell NWs at low temperature (Hua, Motohisa, Kobayashi, Hara, & Fukui, 2008), and more recently in a GaAs/AlGaAs/GaAs core–shell-cap NW at room temperature, as shown in Figure 3.15(a) and (b) (Saxena et al., 2013). However, achieving stimulated emission requires high pump power due to high losses of such lasers. Integration of the NW gain media with external cavities seems a promising route.

Possibilities offered by photonic crystals (PhCs) in terms of light confinement and guidance (Johnson, Mekis, Shanhui, & Joannopoulos, 2001) can lead to tremendous advantages when combined with bottom-up grown NWs. PhC cavities or waveguides on suspended membranes can be used as host substrate for post-positioning of the NW (Birowosuto et al., 2013; Larrue et al., 2012), or SA growing nanopillars to form PhC lasers through the bottom-up approach. For the latter, the PhC laser was fabricated by the SA growth of nanopillars made of GaAs/InGaAs/GaAs axial heterostructure with a GaInP shell on a masked GaAs substrate, as depicted in Figure 3.15(c). Room-temperature lasing action under optical pumping has been demonstrated, with a peak power of 42.5 nW (Figure 3.15(d)). By varying the pillar diameter and interpillar distance, the emission wavelength can be further tuned from 960 to 989 nm (Scofield et al., 2011).

NW is a natural candidate as gain media in LED thanks to their wide range of emission wavelengths (Duan et al., 2000; Fang, Ma, Jaw, Cohen, & Stringfellow, 1990; Hyun et al., 2013; Mattila, Hakkarainen, Mulot et al., 2006). Electrically driven LEDs have been first demonstrated using as-grown GaAs NW with p–n junctions embedded in a transparent dielectric (Haraguchi, Katsuyama, & Hiruma, 1994). A strong emitted light dependence on the polarization has been observed, in accordance with earlier experiments and theoretical predictions (Ruda & Shik, 2005; Wang et al., 2001), paving the way for polarized LEDs (Fang et al., 2011). Single NW emissions have been observed in a transferred InP wire containing an InAsP quantum dot (QD) (Minot et al., 2007; Zwiller et al., 2008) or a free-standing n-GaAs/i-InGaAs/p-AlGaAs core-multishell structure grown on Si substrate (Chuang et al., 2010).

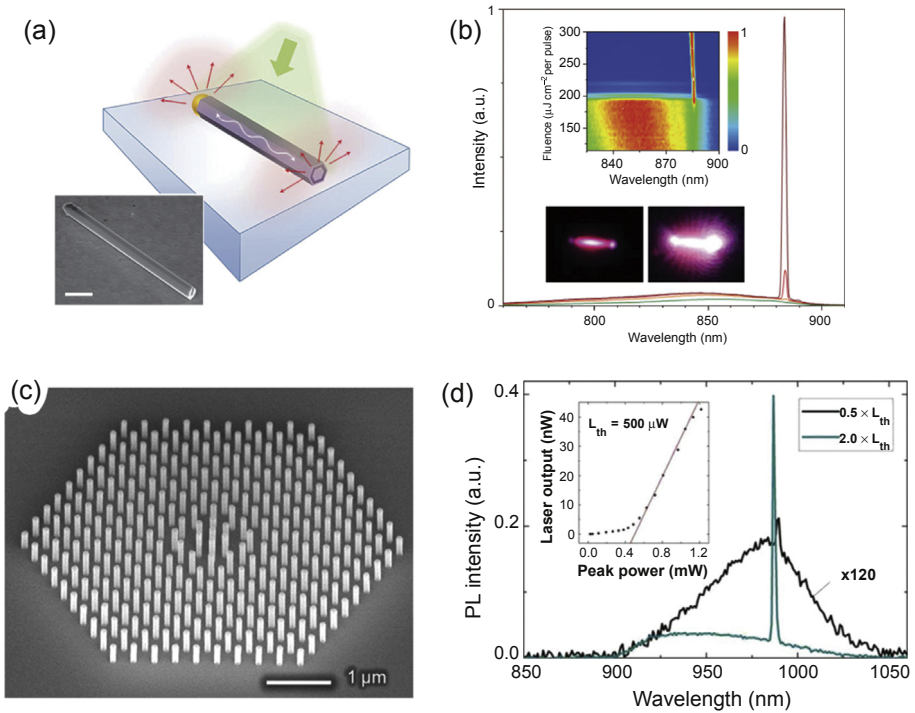


Figure 3.15 (a) Schematic and SEM image of the GaAs NW laser lying on a SiO₂/Si substrate. The NW emits in the near-infrared on the two ends under the 522 nm pulsed laser source pumping. (b) Spectra at four different optical pump powers, showing the transition from spontaneous emission at 144 and 202 μJ/cm² (lower two curves) to lasing at 240 and 288 μJ/cm² (top two). Top inset showing normalized spectral map, and bottom inset displaying optical images of the nanowire below (left) and above (right) threshold. (Adapted by permission from Macmillan Publishers Ltd: Nature Photonics (Saxena et al. (2013). Copyright 2013.) (c) SEM image of a bottom-up grown PhC structure consisting of GaAs/InGaAs/GaAs axial hetero-structured nanopillars passivated by the InGaP shell. (d) The photoluminescence emission of this structure is presented below threshold (curve magnified by 120) and above threshold (exhibiting a sharp peak). Inset shows the output power dependence on the pump power. (Reprinted with permission from Scofield et al. (2011). Copyright (2011) American Chemical Society.)

In addition, a core-multishell GaAs/AlGaAs NW array on Si has been used in LEDs, exhibiting an electroluminescence (EL) threshold current of 0.4 A/cm² at 1.9 V and superluminescence exhibited as the superlinear increment of EL intensity with current injection (Tomioka et al., 2010). Similarly, EL has also been observed in GaAs/InGaP radial heterostructure NW array grown on Si, although the higher intensity of EL emission was reported in the NW array epitaxially grown on GaP substrate (Svensson et al., 2008). To note that no EL from GaP NW has been shown yet, a recent report about direct bandgap WZ GaP NW growth promises further broadening of emission range to the green wavelengths (Assali et al., 2013).

Table 3.2 First orbital Bohr radius of the different non-nitride III–V semiconductor materials

	InP	InAs	InSb	GaP	GaAs	GaSb
a_B (Å)	120	494	1017	50	155	306

Values extracted from [Adachi \(2004\)](#).

The insertion of QD regions and the morphology control during the NW growth makes it possible to tune the spontaneous emission rate in NWs, and thus opens up application in quantum information processing by acting as single-photon sources for the generation of qubits ([Bleuse et al., 2011](#); [Friedler et al., 2009](#)). In earlier studies, bright emission of QDs has been reported in GaP NWs with GaAsP segments ([Borgström, Zwiller, Müller, & Imamoglu, 2005](#)) and in a GaAs NW with InAs QD insertion ([Panev et al., 2003](#)). Single-photon sources using NWs have been reported in several different systems such as AlGaAs NWs with a GaAs QD ([Heinrich et al., 2010](#)), InGaAs QD ([Makhonin et al., 2013](#)), a GaAs NW with an InAs QD ([Claudon et al., 2010](#)), and an InP NW with an InAsP QD ([Reimer et al., 2012](#)).

Thanks to the growth versatility, the diameter of the wires can be tuned to access the quantum regime. The exciton radius (or Bohr radius) expresses the limit at which quantum effects take place in the system, such as radial quantum confinement. This limit can be calculated using the reduced mass and electron mass for each material ([Adachi, 2004](#)). [Table 3.2](#) gives a summary of Bohr radius for the main III–V materials.

The quantum confinement effect has been experimentally studied in single-phase material NWs ([Gudiksen, Wang, & Lieber, 2002](#); [Zhang, Tateno et al., 2009](#)), polytypic NWs ([Pemasiri et al., 2009](#)), and axial heterostructures ([Haraguchi et al., 1994](#)). The measured photoluminescence results are in agreement with those predicted by theoretical investigations: a shift towards lower energy with increasing diameter, along with a strong anisotropic polarization of light absorbed or emitted by NWs ([Ruda & Shik, 2005](#); [Wu, Neaton, & Grossman, 2008](#)). More recently, attention has been paid to the study of nonlinear processes in NWs, such as two-photon absorption-related photoluminescence, or second and third harmonic generation ([Chen et al., 2010](#); [Grange et al., 2012](#); [Wang et al., 2011](#)). A thorough theoretical study of the influence of the wire geometry has shown a strong anisotropy, which differs from one nonlinear process to the other ([Cisek, Barzda, Ruda, & Shik, 2011](#); [Ruda & Shik, 2007](#)). Nonlinearities have been found in wire-like quantum dashes to create a two-photon induced laser ([Capua, Karni, Eisenstein, Reithmaier, & Yvind, 2012](#)), promising potential applications based on nonlinear optical phenomena.

3.3.3 Opto-electronics

With bandgap engineering and controllable doping during bottom-up growth, along with their large surface-to-volume ratio, NWs promise an enhanced sensitivity to light

and become excellent candidates for optoelectronic applications, such as photodetector and photovoltaics (Borgstro et al., 2011; Garnett, Brongersma, Cui, & McGehee, 2011; Hannah et al., 2013; Hyun et al., 2013; Joyce et al., 2011; Soci et al., 2010).

III–V NW direct-bandgap photodetectors gain optical absorption from ultraviolet to infrared. Large-bandgap material (III–N) enables the functionalities in the ultraviolet and visible spectral region, which will not be described here. In 2001, Lieber et al. first reported measurement of integrated photocurrent in a single InP NW (Duan et al., 2001). Following that, an InP photoconductor was demonstrated in nanoneedles grown on a nonsingle crystalline Si platform (Kobayashi et al., 2007), photocurrent spectroscopy was used to study the crystalline structure of a single InP NW at room temperature (Maharjan et al., 2009), and more advanced single-photon detection relying on avalanche amplification of single excitons has been achieved in an InP NW (Bulgarini et al., 2012). The photoconductive response of GaAs systems is also widely investigated, include single GaAs NWs (Kim et al., 2011; Thunich et al., 2009; Wang, 2013), GaAs p–i–n radial structures (Colombo et al., 2009), GaAs/AlGaAs core–shell NWs (Chen et al., 2013; Chuang et al., 2010; Gallo et al., 2011; Jiang et al., 2013; Kim, Dheeraj, Fimland, & Weman, 2013; Persano et al., 2011), and GaAs/InGaP/GaAs core-multishell NWs (Gutsche et al., 2012). Apart from those aforementioned near-infrared light detections (photon energy of 0.9–1.7 eV), narrow bandgap materials (such as InAs) extend the application to the mid-infrared spectral region (photon energy of 0.15–0.4 eV). Though progress of InAs optoelectronic and photonic applications are limited by strong Auger recombination and a nonradiative surface, an InAsP shell could effectively reduce surface recombination and confine the carriers (Pettersson et al., 2006; Treu et al., 2013).

Another promising application lies in solar cells. Planar III–V compound (GaAs) structures can dramatically reduce the material thickness required to absorb 90% of power (optical thickness) to submicron region compared with Si (Kayes, Atwater, & Lewis, 2005). Moreover, NW geometry benefits light harvesting thanks to its long lengths in the direction of incident light, promoting absorption; and small lengths in the radial directions, facilitating carrier collection. Utilizing different III–V materials and heterostructures, a wide range of absorption wavelengths can also be accessible (Goto et al., 2009; Ren et al., 2010; Wei et al., 2009). Single NW solar cells have been experimentally realized in GaAs p–i–n NWs (Colombo et al., 2009; Krogstrup et al., 2013), GaAsP p–i–n NWs (Holm et al., 2013), GaAs/InGaP/GaAs core-multishell NWs (Gutsche et al., 2012), and Schottky contacted GaAs NWs (Han et al., 2012).

Theoretical calculations predict that structures of solar cells affect the light conversion efficiency: dispersed GaAs NWs on host substrate present lower quantum efficiency because of reduced coupling of incident light in the NW (Heiss & Fontcuberta i Morral, 2011), while as-grown GaAs NW solar cells exhibits a theoretical limiting efficiency of 30% (Lapierre, 2011a). Similar trends have been observed in the experimental results. Figure 3.16(a) shows a single p–i–n GaAsP core–shell NW solar cell lying on an SiO₂/Si substrate (Holm et al., 2013). The characterization of this device (Figure 3.16(b)) presents an overall efficiency as high as 10.2%. However, this value is still lower than the theoretically predicted Shockley–Queisser limit of for a semiconductor bandgap of 1.7 eV (Shockley & Queisser, 1961), which

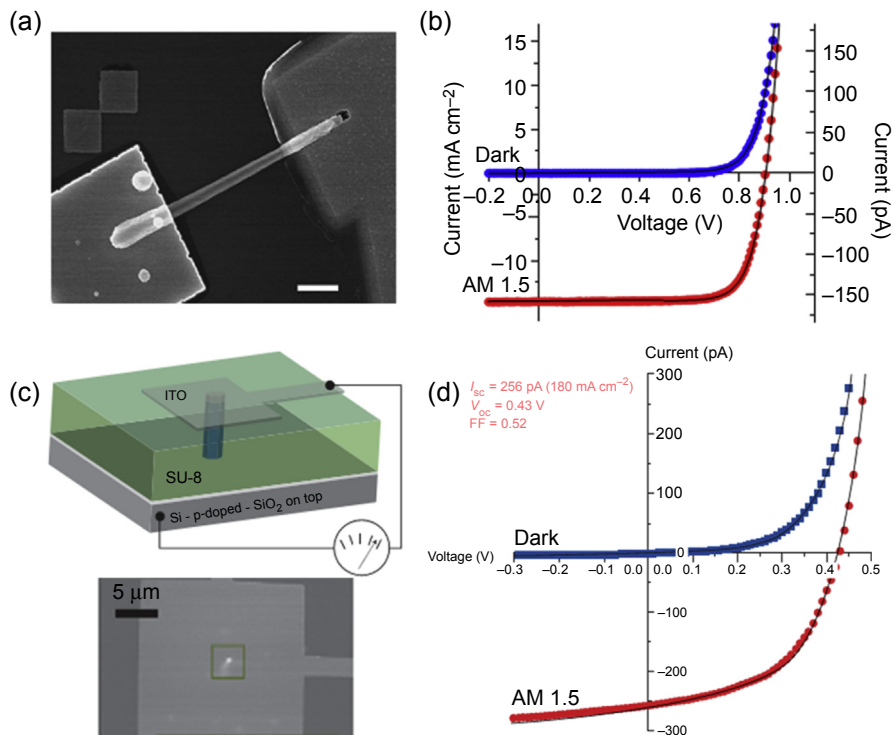


Figure 3.16 Single NW solar cell. (a) SEM image of the device with GaAsP p-i-n core-shell NW connected to metallic pads. Scale bar is 1 μm. (b) I–V characteristics of the device under dark (top curve) and AM1.5G illumination (bottom curve). Data fit is represented in full lines. (Adapted by permission from Macmillan Publishers Ltd: Nature Communications [Holm et al. \(2013\)](#). Copyright 2013.) (c) Schematic of a vertical single NW solar cell consists of a GaAs radial p-i-n NW epitaxially grown on a p-type Si substrate; SEM top view of the device. (d) I–V performance of the device in the dark and under AM 1.5G illumination. (Adapted by permission from Macmillan Publishers Ltd: Nature Photonics [Krogstrup et al. \(2013\)](#). Copyright 2013.)

resulted from the dispersed device configuration. In comparison, a solar cell based on a p-i-n GaAs core-shell NW on p-Si substrate boosts the solar conversion efficiency to 40%, as illustrated in [Figure 3.16\(c\) and \(d\)](#) ([Krogstrup et al., 2013](#)). This remarkable efficiency exceeds the GaAs Shockley-Queisser limit of 33.5% ([Miller, Yablonovitch, & Kurtz, 2012](#)), due to the vertical configuration and enhanced resonant absorption effect.

More recently, devices integrating III–V NW structures heteroepitaxially grown on Si substrates have attracted attention; these are compatible with standard Si technology, and may possibly improve cell efficiency and lower the cost at the same time ([Bu et al., 2013](#); [Foster & Wilson, 2013](#); [Lapierre, 2011b](#)). In combination with NW arrays, the reflectance can be dramatically reduced. Due to strong scattering of the incident light inside the array, more photons are absorbed before being scattered out; this results in

the improved light-trapping properties and absorbance of solar-cell devices (Anttu & Xu, 2013; Muskens et al., 2009; Muskens, Rivas, Algra, Bakkers, & Lagendijk, 2008; Wu, Anttu, Xu, Samuelson, & Pistol, 2012). Meanwhile, NW arrays can also be designed for a certain efficiency and absorption spectral range, since large-diameter NWs absorb light in a longer wavelength region than small diameter, and dense NW arrays reflect less light than sparse arrays (Wu et al., 2012). An array of GaAs NWs grown on an Si substrate has been reported with 8.1% efficiency (Hu et al., 2013), along with an InAs NW array grown on Si that exhibited a 2.5% efficiency (Wei et al., 2009). GaAsP core-shell n-p junction grown on a (001)-oriented Si substrate have also shown photovoltaic properties (Tchernycheva et al., 2012).

A better understanding of performance limitations in terms of inherent physical properties and NW growth and device structure design, will certainly lead to a wide use of III-V NW devices.

3.3.4 Quantum transport

NWs enable the formation of abrupt, defect-free interfaces between lattice-mismatch semiconductors, which opens up new opportunities for the fundamental investigations of low-dimensional quantum devices based on III-V heterostructures.

Tunnel diodes are key components in multijunction solar cells, low-power memory devices, and low-power tunnel FETs (TFETs). III-V NW tunnel diodes based on staggered (InAs/Si (Bessire et al., 2011; Björk et al., 2010), InP/GaAs (Wallentin et al., 2010), InAs/InP (Björk, Ohlsson, Thelander, et al., 2002)) and broken (GaSb/InAs (Borg et al., 2012)) type-II band alignment were investigated in details in terms of tunnel process and impact of traps from defects and dislocations at the junction interface.

In conventional FETs, carrier transport is limited by thermionic injection. SS is defined as:

$$SS = \left[\frac{d(\log_{10} I_D)}{dV_G} \right]^{-1} \quad (3.3)$$

where $\ln 10 \cdot \frac{kT}{q} \cong 60 \text{ mV}$. As a result, the minimum SS will be 60 mV/dec, indicating that traditional FETs require at least 60 mV of gate voltage to increase the current density by one order of magnitude. In comparison, carrier transport in TFETs follows band-to-band-tunneling (BTBT) through the space charge region of the junction, resulting possibly in an SS lower than 60 mV/dec. Note that SS is constant over a smaller applied gate-source bias (Ionescu & Riel, 2011) when compared to conventional FETs. As a result, lower supply voltage and power consumption are required. However, TFETs usually suffer from low On current, which can be overcome by using III-V NWs, since their low effective-mass and band engineering are expected to increase the transmission probability, and then On current (Ionescu & Riel, 2011). Superior electrical transport performance has been successfully demonstrated in TFETs based on InAs NWs on Si (lowest SS = 21 mV/dec) (Ionescu & Riel, 2011; Riel et al., 2012; Tomioka & Fukui, 2011; Tomioka,

Table 3.3 Direct bandgap energy for the two crystalline phases, common dopant element and main applications of the different undoped non-nitride III–V nanowire materials

Material	Direct bandgap energy (eV)		Main applications
	ZB	WZ	
InP	@0 K 1.42 Vurgaftman, Meyer, and Ram-Mohan (2001), Mishra et al. (2007), and Ikejiri, Kitauchi, Tomioka, Motohisa, and Fukui (2011) @300 K (1.34–1.35) Adachi (1989) and Madelung (2004)	@0 K (1.47–1.50) De and Pryor (2010), Mishra et al. (2007), and Ikejiri et al. (2011) @300 K 1.43 Mishra et al. (2007)	Laser: InP/InAs/InP axial heterostructure Birowosuto et al. (2013). LED: InP with InAsP quantum dot Minot et al. (2007). Single-photon source: InAsP QD in InP NW Reimer et al. (2012). Quantum effect: InP Gudiksen, Wang et al. (2002), polytypic InP Pemasiri et al. (2009). Nonlinear processes: InP Wang et al. (2011). Photodetector: InP Kobayashi et al. (2007). Single-photon detector: InP Bulgarini et al. (2012). NWFET: InP Storm, Nylund, Borgstrom et al. (2011). Tunnel diode: InP/GaAs axial heterostructure Wallentin et al. (2010). TFET: n-InP/p-GaAs axial heterostructure Ganjipour, Wallentin et al. (2012).
InAs	@0 K 0.42 Fang et al. (1990) and Vurgaftman et al. (2001) @300 K (0.35–0.36) Adachi (1989), Vurgaftman et al. (2001)	@0 K (0.47–0.48) De and Pryor (2010), Zanolli, Fuchs, Furthmüller, Von Barth, and Bechstedt (2007)	Photodetector: InAs/InAsP axial heterostructure Pettersson et al. (2006). Solar cell: InAs Wei et al. (2009). NWFET: InAs Dayeh, Aplin et al. (2007), Thelander et al. (2011), Ford et al. (2010), Dey et al. (2012), and Storm, Nylund, Samuelson et al., 2011, InAs/InP core–shell Jiang et al. (2007), InAs/InAsP/InAs axial heterostructure Lind et al. (2006), vertical InAs Tanaka et al. (2010), Rehnstedt et al. (2008), Bryllert et al. (2006), and Thelander et al. (2008). Tunnel diode: InAs NW on Si Bessire et al. (2011) and Björk et al. (2010), InAs QD bounded with InP barrier in InAs NW Björk, Ohlsson, Thelander et al. (2002). TFET: InAs NW on Si Tomioka et al. (2012b), Tomioka and Fukui

Continued

Table 3.3 Continued

Material	Direct bandgap energy (eV)		Main applications
	ZB	WZ	
InSb	@0 K 0.24 Littler and Seiler (1985) and Adachi (2004) @300 K (0.17–0.18) Adachi (1989) , Littler and Seiler (1985) , Vurgaftman et al. (2001) , and Madelung (2004)	@0 K 0.287 De and Pryor (2010)	(2011), Riel et al. (2012) , and Ionescu and Riel (2011) . SET: InAs QD bounded with InP barrier in InAs NW Thelander et al. (2003) . IR detector: InSb Dey, Svensson et al. (2013) . NWFET: p-InSb Yang et al. (2013) . Superconductor: InSb Tomioka, Yoshimura, and Fukui (2013) , InSb nanocrosses Plissard et al. (2013) .
GaP	@0 K 2.866 Zollner et al. (1993) @300 K 2.76(mean value) Zollner et al. (1993) ^a	@0 K (2.09–2.11) Assali et al. (2013)	Single-photon source: GaAsP segments in GaP wire Borgström et al. (2005) .
GaAs	@0 K 1.52 Vurgaftman et al. (2001) , Blakemore (1982) , Madelung (2004) , and Adachi (2004) @300 K (1.42–1.44)	@0 K (1.50–1.55) De and Pryor (2010) , Ketterer et al. (2011) , and Murayama and Nakayama (1994) @300 K 1.39 Ketterer et al. (2011)	Laser: InGaAs/GaAs core–shell Chen et al. (2011) , GaAs/GaAsP core–shell Hua et al. (2008) , GaAs/InGaAs/GaAs axial heterostructure with GaInP shell Scofield et al. (2011) . LED: p-n junction GaAs nanowire Haraguchi et al. (1994) , GaAs/InGaP radial heterostructure Svensson et al. (2008) , GaAs/AlGaAs core-multishell Tomioka et al. (2010) . Single-photon source: InAs quantum dot in GaAs nanowire Claudon et al. (2010) and Panev et al. (2003) , AlGaAs with GaAs QD

GaSb	Blakemore (1982) and Adachi (1989) @0 K (0.81–0.82) Vurgaftman et al. (2001), Madelung (2004), and Adachi (2004) @300 K (0.72–0.75) Adachi (1989) and Vurgaftman et al. (2001), Madelung (2004), and Adachi (2004)	@0 K 0.509 De and Pryor (2010)	Heinrich et al. (2010), InGaAs QD in GaAs NW Makhonin et al. (2013), Quantum effects: GaAs Zhang, Tatenio et al. (2009), P-n junction GaAs Haraguchi et al. (1994). Nonlinear processes: GaAs Grange et al. (2012) and Chen et al. (2010). Photodetector: GaAs/InGaP/GaAs core-multishell Gutsche et al. (2012), GaAs/AlGaAs core–shell Gallo et al. (2011), GaAs Wang (2013), avalanche in GaAs-based heterostructure Chuang et al. (2010). Solar cell: P-i-n GaAs Krogstrup et al. (2013) and Colombo et al. (2009), p-n radial GaAs (Czaban, Thompson, and Lapierre (2008), GaAs/GaInP/GaAs core-multishell Gutsche et al. (2012), GaAs Han et al. (2012) and Hu et al. (2013), GaAs/GaInP core-multishell Nakai, Yoshimura, Tomioka, and Fukui (2013), p-i-n GaAsP core–shell Holm et al. (2013), GaAsP core–shell Tchernycheva et al. (2012). NWFET: GaAs Schricker et al. (2006) and Fortuna and Li (2009). Tunnel diode: GaSb/InAs(Sb) axial heterostructure Borg et al. (2012). TFET: GaSb/InAs(Sb) axial heterostructure Dey, Borg et al. (2013). SHT: p-type GaSb Ganjipour et al. (2011).
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^aIndirect energy–gap for intrinsic material.

Yoshimura, & Fukui, 2012b), InP/GaAs heterostructure NWs (highest $I_{\text{on}}/I_{\text{off}} = 10^7$) (Ganjipour, Wallentin, Borgström, Samuelson, & Thelander, 2012), and GaSb/InAs NWs (maximum drive current of $310 \mu\text{A}/\mu\text{m}$ for $V_{\text{DS}} = 0.5 \text{ V}$ at RT, lowest SS of 17 mV/dec at 4.2 K) (Dey, Borg, et al., 2013).

At the same time, intense efforts have been carried out on single-electron transistors (SETs), where one electron at a time tunnels through a small island connected to two leads via tunnel junctions. It can be used for sensitive charge detectors, spintronics, and quantum computation. An InAs(QDs)/InP(barrier) NW-based SET exhibited a Coulomb blockade single-island transistor signature at liquid helium temperature (4.2 K), which was not observed in homogeneous InAs NWs (Thelander et al., 2003). In the case of a single-hole transistor (SHT), Ganjipour et al. demonstrated a p-type GaSb NW with close source/drain contacts that showed an infinite resistance for V_{DS} between -5 mV and 5 mV , while a series of Coulomb peaks were detected as a function of back-gate voltage at $V_{\text{DS}} = 0.1 \text{ mV}$.

3.4 Conclusion

III–V nanowire bottom-up growth mechanisms and methods are summarized. A comprehensive understanding of their crystallographic properties (i.e., defects, doping, homo- and heterojunctions, and heteroepitaxial growth) paves the way for diverse applications in electronics, photonics, optoelectronics, and quantum transport. The fundamental studies and superior performance demonstrated in single-nanowire devices opens up possibilities in large-scale nanowire device integration when combined with selective-area growth, aiming at transferring technology from the laboratory to practical implementations.

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III–V semiconductor nanowires: nitrides (N-based; III-N)

4

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4.1 Introduction: the importance of III-nitride alloys

The share of GaN-based alloys semiconductor devices in the total semiconductor device market is expected to rapidly expand in the years to come as stated in a report by Transparency market research (marketsandmarkets.com, 2014). The emergence of new technologies and growing application areas are the major drivers of the GaN-based alloys market. Growing need for power efficient semiconductor devices coupled with increasing application areas, especially in the field of computers, information and communication technology, consumer electronics, and the automotive and industrial sectors has strengthened the growth of the GaN semiconductor devices market. In the automotive sector, GaN-based alloy light-emitting diodes (LEDs) have already started replacing incandescent lamps. In the consumer electronics sector, the rising demand for fixed and wireless devices such as TVs, laptops, gaming devices, and smartphones is expected to drive the GaN semiconductor device market. In the future, consumer electronics will be one of the largest market areas and is expected to remain in a dominant position during the forecast period 2013–2019, while power semiconductors show the fastest growth potential during this period. The worldwide GaN LED market rose up to 12.4 billion U.S.\$ in 2013 driven by surging demand from the lighting, tablet, and mobile phone backlighting segments, and it will increase in the coming years. This development is especially driven by growth and advances in the sectors of solid-state lighting and laser technology of GaN-based alloys.

The III-nitrides are a class of direct bandgap semiconductors, consisting of GaN (bandgap 3.4 eV) (Morkoc, 2008), InN (0.63 eV) (Davydov et al., 2002), and AlN (6.2 eV) (Morkoc, 2008). By appropriate alloying, an extended wavelength range from the near infrared into the visible and up to the ultraviolet can be covered. This makes the III-nitrides ideal materials for applications as LEDs, semiconductor laser diodes (LDs), and light detectors.

Motivated by the first demonstration of the ultraviolet/blue LEDs and LDs in 1997 by Nakamura (1996b), many research groups worldwide strongly pursued GaN research activities in the optoelectronic field. Among other achievements, they have succeeded in the fabrication and development of longer emission wavelength LEDs and LDs, particularly green ones (Avramescu et al., 2010; Funato, Kim, Ochi et al., 2013; Khan, 2009; Nakamura, 1996a; Okamoto et al., 2009; Takagi et al., 2012; Viswanath, 2014). However, though green LDs have started to be commercialized, they exhibit internal quantum efficiencies far below the ones of blue LDs

(Crawford, 2009; Khan, 2009; Ohta, DenBaars, & Nakamura, 2010; Raring et al., 2010). This issue may be related to poor optical confinement and/or alloy fluctuations (Funato, Kim, Hira et al., 2013; Skierbiszewski et al., 2013), as the active regions of these devices require (In,Ga)N with higher In content. For extending the spectral range of light emitters into the deep ultraviolet range, AlN and (Al,Ga)N alloys with high Al content are ideal candidates (Adivarahan et al., 2004; Jmerik et al., 2008; Nikishin et al., 2003; Taniyasu, Kasu, & Makimoto, 2006) since AlN possesses the largest direct bandgap of known semiconductor materials. Alloying of AlN with InN and GaN allows tuning the energy gap and the valence and conduction band offsets over a wide range. The deep UV spectral region is of interest to realize light sources to be used in important applications such as biological agent detection, water purification, and medical equipment decontamination and sterilization.

4.2 III-nitride nanowires: brief historical overview

Production of III-nitride native substrates is a considerable challenge mainly linked to the very large vapor pressure of N, coupled with a low solubility of N in the metal melts at reasonable temperatures and pressures. Most severe is the InN case followed by AlN and to a lesser extent by GaN due to the considerable efforts to produce it. Thus, typically one resorts either to very thick (100 μm) GaN layers grown by hydride vapor phase epitaxy (HVPE) or to high quality heterosubstrates. However, in the latter cases there is a substantial thermal and lattice mismatch causing tensile or compressive strain, and this can result in defects in the grown layer. Therefore, III-nitride-based devices show high densities of defects that can reduce device performance. The lack of a suitable homo- or heterosubstrate is one of the main reasons for the late development of III-nitride alloys that only from the 1990s onward have been subjected to considerable progress. Accordingly, interest in the growth of nitride nanowires (NWs) has lagged behind other NWs. The first report on GaN needles was made by Dingle (1971), with diameters of the order of tens of microns, but significant research activity in this field starts only at the end of the 1990s. In 1997 by reacting Ga₂O with NH₃ Han et al. synthesized GaN NWs inside carbon nanotubes (Han, 1997). The research groups of Kishino (Yoshizawa et al., 1997) and Calleja (Sanchez-García et al., 1998) reported the growth of GaN NWs by plasma-assisted molecular beam epitaxy (PA-MBE) under N-rich conditions without the use of a foreign catalyst. Excellent structural and optical properties were achieved (Calleja et al., 2000).

The first report of GaN MBE NW growth by the vapor—liquid—solid (VLS) mechanism using a foreign metal particle was published by Mamutin (1999).

Despite the initial low scientific interest, III-nitride NWs have great potential in optoelectronic applications. The small lateral size of the NWs reduces the problem of lattice mismatch because strain relief by elastic deformation is easier in NWs and facilitates the incorporation of heterostructures. The superior crystalline quality of NWs and the increased freedom in bandgap engineering can drastically improve the device performance as shown by the demonstration of new nanoelectronic devices including optoelectronic nanodevices (Huang et al., 2002; Johnson et al., 2002).

Numerous methods have been developed to produce III-nitride NWs, of which the most prominent, chemical vapor deposition (CVD) and PA-MBE, will be briefly discussed in the next; the treatment of NW growth and synthesis is discussed in more detail in Part II. In most of the cases, however, what all these approaches have in common is that the NWs are deposited on a substrate either by catalyst-assisted methods taking advantage of the VLS mechanism (Wagner et al., 1964) or by a catalyst-free self-assembled approach.

In the CVD method the reaction of Ga with ammonia was used to produce single crystalline wires with few defects (Chen et al., 2001; Johnson et al., 2002). Catalytic growth using metalorganic vapor phase epitaxy (MOVPE) (Kuykendall et al., 2003) with trimethylgallium, trimethylindium, and ammonia allowed the creation of high-density arrays of III-nitride NWs. Different reaction parameters were applied to systematically optimize and control the VLS growth. In addition, an appropriate substrate selection was used to control the crystallographic growth directions of NWs (Kuykendall et al., 2003) with distinct geometric (triangular or orthogonal cross-section) and physical properties (different polarization fields).

PA-MBE is in general not regarded as the fabrication methodology of choice for III-nitride-based technology. The lack of high nitrogen overpressure required for the optimum growth temperature of nitrides (1050 °C for GaN) is considered as the major issue. In contrast, PA-MBE fabrication of NW structures with device quality becomes possible at much lower growth temperatures (720–750 °C) in N-rich conditions by the self-assembled nanostructure growth.

4.3 GaN nanowires

Controlled growth of GaN NWs by MOCVD requires the use of metal nanoparticles as catalysts within the general context of the VLS growth to control the critical nucleation and subsequent elongation steps of NW growth (Morales & Lieber, 1998). It was demonstrated that NW diameter is indeed controlled by the size of the nanoparticle catalyst as suggested by the growth model; the NW length is proportional to the growth time, and specific dopants can be incorporated into NWs to control their electronic properties (Zhong et al., 2003). Using this approach, C. M. Lieber's group concentrated on the synthesis of core/multishell NW heterostructures to produce tunable multicolor nanophotonic sources (Li et al., 2006; Qian et al., 2004, 2005). Core/multishell NWs were prepared by MOCVD with n-GaN core and (In,Ga)N/GaN/p-(Al,Ga)N/p-GaN shells, where variation of indium mole fraction was used to tune the emission wavelength. These NWs are dislocation-free single crystals with a triangular morphology.

Similar triangular morphology of GaN NWs was also obtained by P. D. Yang's group (Kuykendall et al., 2003). The work was extended by synthesizing GaN NWs via metal-initiated MOCVD on silicon and sapphire substrates. The wires were formed via VLS mechanism with gold, iron, or nickel catalysts. Following these initial investigations, researchers have studied in more detail the correlation between the growth temperature and photoluminescence in GaN NWs grown with metal-catalyzed MOCVD (Talin et al., 2008).

In 2003, the first direct observation of self-catalytic growth of GaN NWs via VLS mechanism was achieved (Stach et al., 2003). For that purpose, GaN was decomposed at high temperature in vacuum, which yields nanoscale Ga liquid droplets and Ga/N vapor species for the subsequent GaN NW nucleation and growth. After that observation, researchers focused on the investigation of catalyst-free growth of GaN NWs by MOCVD (Tessarek, Bashouti et al., 2013; Tessarek, Dieker et al., 2013; Tessarek, Sarau et al., 2013; Tessarek et al., 2014). GaN NWs produced in this way exhibited diameters from a few μm down to 100 nm (Tessarek, Bashouti et al., 2013). Structural investigations showed that larger GaN NWs (diameter >500 nm) contained threading dislocations in the bottom part and vertical inversion domain boundaries, which separate a Ga-polar core from an N-polar shell. In contrast, small GaN nanorods (200 nm) were largely free of such extended defects. It was also shown that density, height, and diameter are strongly influenced by the growth time (Tessarek, Dieker et al., 2013). A deposition time of a few minutes has led to the formation of GaN NWs, and increasing the time up to 1 h resulted in the formation of NWs with heights exceeding 47 μm . In dependence on the crystallographic orientation of the sapphire substrate (c-, a-, m-, r-plane sapphire), vertical, tilted, and in-plane GaN NWs were achieved (Tessarek et al., 2014). Most of the vertically aligned NWs exhibited a regular hexagonal shape with sharp edges and smooth side facets leading to whispering gallery modes with high-quality factors demonstrating the high morphological and optical quality of the self-assembled GaN NWs grown by MOCVD (Tessarek, Sarau et al., 2013).

Self-assembled GaN NWs grown with MBE are virtually free of threading dislocations that form during growth of GaN films and are not affected by the mismatch in the thermal expansion coefficients between GaN and Si. Consequently, the crystal quality of these GaN NWs is very high (Brandt et al., 2010; Stoica et al., 2008).

The crystal quality and the optical quality of NWs are some of the most crucial parameters as they essentially determine the device efficiency. Growing GaN NWs by MBE at lower substrate temperatures (e.g., below 800 $^{\circ}\text{C}$) has led to an enhanced coalescence of NWs and formation of NW aggregates that have been formed by the coalescence of several single NWs (Dogan, Brandt, Pfüller, Bluhm et al., 2011). This unintentional coalescence was caused both by the high density of NWs formed at lower substrate temperatures and by the non-negligible tilt of the NWs with respect to substrate surface. As a consequence, this unintentional coalescence resulted in formation of stacking faults at the coalescence boundary of two adjacent NWs (Consonni et al., 2009). The optical quality of the NWs grown at lower substrate temperatures was worse as reflected by a larger full-width-at-half-maximum (FWHM) of donor-bound-exciton transition at 3.472 eV investigated by low temperature microphotoluminescence ($\mu\text{-PL}$) measurements. With increasing substrate temperature (e.g., above 800 $^{\circ}\text{C}$), the density of NWs decreased and hence the degree of this unintentional coalescence was reduced. For example, GaN NWs grown at 820 $^{\circ}\text{C}$ exhibited an average diameter of 30 nm and a density of about 10^{10} cm^{-2} with a very narrow FWHM of donor-bound-exciton transition of 1.6 meV (Figure 4.1).

Another important characteristic for successful device processing is a homogeneous height distribution of the NW array. Several studies were concerned with the length distribution of GaN NWs (Debnath et al., 2007) by MBE grown at identical conditions

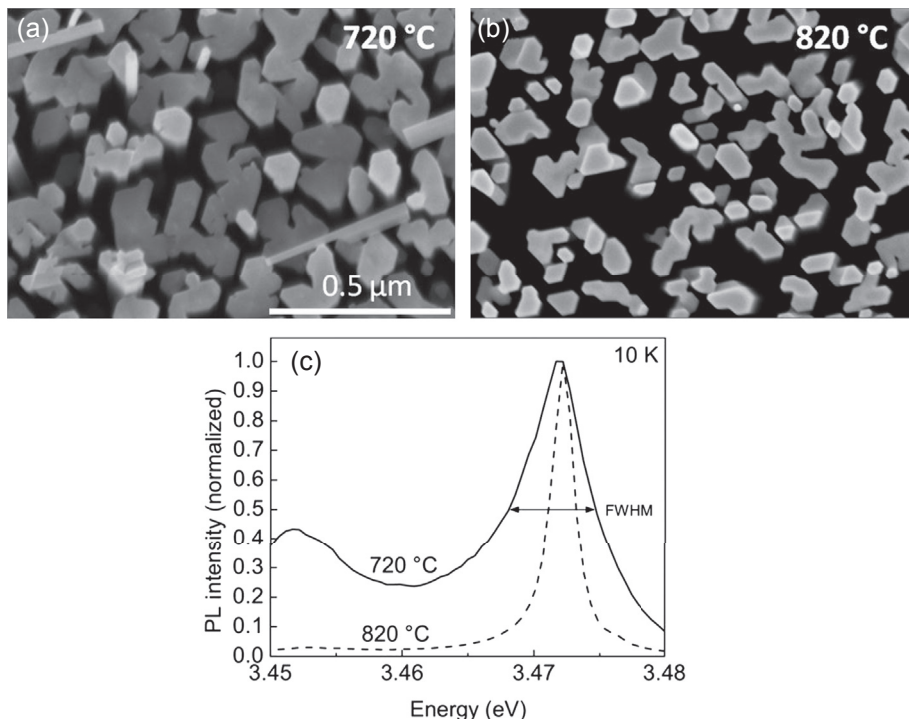


Figure 4.1 Top-view scanning electron microscope (SEM) images of GaN NWs grown at (a) 720 °C and (b) 820 °C, respectively, and (c) their corresponding low-temperature μ -PL spectra.

but for different durations (Calarco et al., 2007). GaN NWs grown for a shorter time (e.g., 1 h) exhibited a fairly wide length distribution. Some of the NWs were significantly longer than those in their neighborhood. This was attributed to the different nucleation times of the GaN NW nuclei. In contrast, GaN NWs grown for a longer time (e.g., 3 h) revealed a surprisingly homogeneous length distribution. This was mainly explained by the fact that Ga atoms desorbed from the side surfaces of NWs readsorb on neighboring NWs (Sabelfeld et al., 2013). This process favored the growth of shorter NWs and gave rise to a narrow NW height distribution during the late stages of the growth. With respect to the V/III flux ratio, the lateral growth of NWs in comparison to their axial growth was investigated (Fernández-Garrido et al., 2013).

Another important advantage in using GaN NWs for device application relates to the possibility of choosing their polarity. Due to the choice of substrate orientation or to the growth conditions, it is possible to obtain Ga-polar (Brubaker et al., 2011), N-polar (Fernández-Garrido et al., 2012), or nonpolar (Kuykendall et al., 2003) top surfaces. N-polar top surfaces for instance are particularly interesting because of much higher In incorporation on such surfaces especially relevant for establishing a green LED. (In,Ga)N-based LEDs emitting in the UV- and blue-wavelength range are already available on the market. More than 50% external quantum efficiencies (EQE) have been achieved for blue LEDs with both c-plane and semipolar orientations, whereas the

maximum EQE reported for a green LED is 30% (Zhao et al., 2010). One of the main reasons for the decreasing efficiency for longer wavelengths is that emitters for green and longer wavelengths still pose significant growth and device design challenges. Firstly, due to the higher volatility of In species, the growth of conventional Ga-polar (In,Ga)N requires lower growth temperatures than the optimal growth temperature of GaN. This mismatch in optimal growth temperatures leads to challenges in the growth of high quality (In,Ga)N/GaN multiple quantum well (MQW) emitters. Secondly, polarization effects are more pronounced as the In composition is increased. It is expected that the relatively high polarization fields in c-plane-oriented (In,Ga)N/GaN emitters could lead to poor carrier confinement and consequently poor efficiency in LED structures. The N-polar orientation of GaN has several advantages to make it attractive for high In content (In,Ga)N growth. N-polar InN can be grown at higher temperatures than In-polar InN (Xu & Yoshikawa, 2003). This is attributed to the higher stability of InN on the N-polar surface. Recent work on N-polar (In,Ga)N growth demonstrated significantly higher growth temperatures and In incorporation on N-polar (In,Ga)N when compared to Ga-polar (In,Ga)N (Nath et al., 2010). The direction of the spontaneous and piezoelectric polarization in N-polar is reversed from that of Ga-polar surface, which may provide advantages for LED operations.

4.3.1 NW positioning

The selective area growth (SAG) of GaN NWs enables the benefit of having control over the NW radius, position, and pitch for subsequent device processing.

One of the most prominent results was achieved by MOCVD by Hersee, Sun, and Wang (2006; Hersee et al., 2009; Wang et al., 2006). Arrays of GaN NWs with uniform size and longer-range positional order were grown by MOCVD using conventional precursors with no additional catalyst (Wang et al., 2006). The location, orientation, and diameter of each GaN NW were controlled using a thin, selective silicon-nitride growth mask that is patterned by interferometric lithography onto mainly SiC substrates (Hersee et al., 2006). An important and novel feature of that process was that the NW diameter remains constant after the NWs have merged from the selective growth mask.

Waag et al. also intensely investigated the growth of GaN NWs by MOCVD. In 2008, they initially focused on growing GaN-based heterostructures on three-dimensionally patterned Si(111) substrates with the goal of fabricating well-controlled, high-quality, defect-reduced GaN-based nano-LEDs (Fündling et al., 2008). A pronounced dependence of the morphology of the GaN structures on the size and pitch of the Si pillars was found. Later, to eliminate the parasitic growth of GaN on the mask, they employed AlN/Si substrates. TEM measurements revealed that the threading dislocations bend to the side facets of the GaN nanostructures and terminate (Li et al., 2010). The group's recent studies focused on the position-controlled growth of GaN NWs on sapphire substrates (Bergbauer et al., 2011) with a special focus on the influence of polarity (Li et al., 2012; Wang et al., 2012, 2013) and a potential future application as core-shell NW LED structures (Mandl et al., 2013; Waag et al., 2011).

Gradečak et al. focused on the growth of GaN NWs by using a catalyst in MOCVD. The influence of the Au-catalyst particle on the growth properties of such GaN NWs was investigated in detail (Crawford, Lim, & Gradečak, 2012; Lim, Crawford, & Gradečak, 2010). Recently their work demonstrated the growth of unique GaN/AlN MQW NWs by using nickel nanocluster-mediated VLS growth and correlated the observed blue-shifted luminescence in PL to the size-associated confinement effect in QW structure (Qian et al., 2012).

In 2001, Gupta et al. successfully obtained the first SAG of GaN with MBE (Gupta et al., 2000). While the first achievement of SAG of GaN NWs by MBE was reported in 2003 (Kawasaki et al., 2002), it required more than five years until new publication of research followed (Calleja et al., 2007; Ishizawa et al., 2007). In contrast to the SAG of GaN by ammonia MBE (Kawasaki et al., 2002) where the selectivity results from different cracking efficiencies on the mask and the substrate, the understanding of the selectivity mechanism for PA-MBE is still under discussion in the literature.

Kishino et al. obtained SAG at high temperatures and high Ga fluxes on AlN dots on a Si(111) substrate (Sato et al., 2006). They observed that the AlN acts as a nucleation site and the driving selective mechanism is the diffusion from the substrate to the AlN dots. The nucleation on the mask for a given temperature regime around 941 °C is not completely suppressed, while it is in the case of temperatures higher than 966 °C. In work that followed, the authors focused on the homoepitaxy of GaN NWs on GaN templates using Ti-masks (Sekiguchi, Kishino et al., 2008). Using this approach, the NW morphology was clearly improved.

Calleja et al. (2007) employed a SiO_x mask on a Si(111) substrate. After the growth, the SiO_x mask was selectively etched and possible material grown on the mask was thus stripped. Therefore, the selectivity for this approach is not crucial.

Bertness et al., (2010) fabricated SAG GaN NWs with a Si₃N₄ mask grown on an AlN-buffered Si(111) substrate. They ascribed the driving force for the SAG to the different sticking coefficient of the adatoms on the substrate and mask. Following this argument, one can conclude that the selectivity is strongly influenced by Ga desorption.

In previous publications Calarco et al. reported on the selective growth of GaN NWs grown by MBE in holes of a patterned silicon oxide mask prepared by standard e-beam lithography establishing and demonstrating optimum growth conditions (Schumann et al., 2011a, 2011b). The adatom diffusion mechanism was intensely investigated, highlighting its significant role for the growth kinetics of selectively grown GaN NWs (Gotschke et al., 2011).

4.3.2 Microcrystals born from NWs

Today, the fabrication of these μ -size devices is mainly based on a top-down approach by etching the planar III-nitride structures to define the μ -size. The performance of all devices fabricated in this way is, in principle, limited by structural defects present in the as-grown films caused by the large lattice mismatch between GaN and Si and by defects generated by the required processing steps. As an alternative to the top-down approaches used today, a bottom-up approach based on the pendeoepitaxial expansion and coalescence of selectively grown GaN NWs for the fabrication of GaN films on

foreign substrates was first suggested by Kusakabe, Kikuchi, and Kishino (2001). In this technique, first GaN NW ensembles are produced either by direct epitaxial growth on the substrate or, more frequently, by etching GaN nanopillars from a GaN film. Later, by changing the growth conditions, the lateral growth is promoted such that the top areas of NWs undergo coalescence by pendeoepitaxy. In previous work, this technique had been successfully demonstrated initially for sapphire substrates (Chao et al., 2009; Cherns et al., 2010) and then recently for Si substrates (Bougrioua et al., 2007; Dogan, Brandt, Pfüller, Lähnemann et al., 2011; Kato et al., 2009). Work on Si substrates includes reports on lasing from GaN microdisks pivoted on Si (Choi et al., 2006) and GaN-based microdisk LEDs on nanosilicon-on-insulator templates (Tripathy et al., 2008). The pendeoepitaxial overgrowth technique has the potential of decreasing the dislocation density of the overgrown GaN film on Si substrates, which would improve the performance of the devices like LEDs (Feltin et al., 2003).

Normally, GaN NWs are grown in MBE under N-rich conditions, giving them their three-dimensional shape and high aspect ratio. In contrast, for growing GaN planar structures, Ga-rich growth conditions are preferred. A two-step experiment using both growth conditions was performed. In a first step, a GaN NW array under N-rich conditions with a fairly wide height distribution was grown. Later, the growth conditions were shifted toward Ga-rich to be able to promote lateral growth of GaN NWs. This process enabled the pendeoepitaxial overgrowth of GaN NWs. Since the initial GaN NW template had a fairly wide height distribution, longer NWs had a greater chance to collect the impinging atoms and therefore grow faster laterally. This resulted in formation of GaN μ -crystals with a size of 1–3 μm (Figure 4.2(a)) (Dogan et al., 2011). With careful SEM and TEM investigations it was shown that these GaN μ -crystals were formed by the pendeoepitaxial overgrowth of a single NW that is longer than its immediate neighbors. GaN μ -crystals exhibited an atomically flat c-plane surface with side facets. Most importantly, these GaN μ -crystals are entirely free of dislocations. The single crystalline nature of the GaN μ -crystals manifested itself in excellent optical properties as well. Cathodoluminescence measurements have shown that the emission of the μ -crystals is strong and perfectly homogeneous, reflecting the absence of threading dislocations as well. The optical quality of the μ -crystals has been further investigated by μ -PL measurements. The FWHM of the donor-bound-exciton transition at 3.471 eV was found to be 1 meV (Figure 4.2(b)). This value is not much larger than that of the state-of-the-art free-standing GaN template (0.6 meV) prepared by HVPE.

For comparison, the donor-bound-exciton transition of ammonothermally grown GaN (a method of producing bulk GaN crystals—an alternative to sapphire templates used for flip-chip-bonding today) has been reported to be spectrally located 5 meV higher than 3.471 eV (compressive strain) with the narrowest FWHM of 0.46 meV (Bai et al., 2004). Moreover, the width of 1 meV for the donor-bound-exciton transition of the GaN μ -crystal is significantly narrower than that of typical GaN films on Si(111) (10–20 meV). To our knowledge, this is the best PL line width obtained for an extended GaN crystal grown by MBE on any substrate. The GaN μ -crystals on Si exhibit a structural and optical quality comparable to that of a state-of-the-art free-standing GaN reference sample.

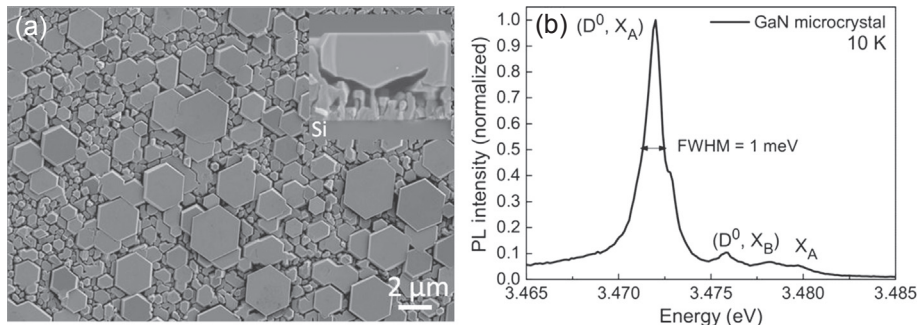


Figure 4.2 (a) Top-view scanning electron microscope image of GaN microcrystals obtained by the pendeoepitaxial overgrowth of GaN NWs (inset shows the cross-sectional view); (b) low-temperature μ -PL spectrum of a GaN microcrystal.

We believe that the improved properties of GaN μ -crystals make them a perfect candidate to be used as a template for the growth of (In,Ga)N/GaN μ -LEDs on Si. The microphotonic technologies may provide the ability to integrate arrays of thousands of low-cost optical circuit elements such as light sources on a single chip. Nitride-based microphotonic structures, including μ -size disks, rings, pyramids, prisms, and optically pumped vertical cavity surface emitting laser structures with feature sizes down to submicrometers have been explored (Li et al., 2000; Mair et al., 1998). The fact that these GaN μ -crystals arising from NWs are dislocation-free brings a strong competition to form μ -LED structures against their counterpart approaches based on etching GaN films on Si, which are known to contain a considerable number of threading dislocations.

4.4 (In,Ga)N alloy and heterostructure nanowires

As mentioned in the introduction, (In,Ga)N alloy is the heart of many devices and particularly of solar cells and light emitters with wavelength in the visible spectral range beyond blue (450 nm). However, the fabrication of heterostructures with high In content is needed to get longer emission wavelength. This results in a particularly demanding task. The large lattice mismatch between the binary InN and GaN exceeds 11% (Ng et al., 2002), and the much larger N equilibrium pressure required to stabilize InN compared to GaN (Ambacher, 1996) results in a large difference in the optimum growth temperature for InN and GaN, respectively. As a consequence, In compositional inhomogeneity and phase separation usually occur for large In content (In,Ga)N. Hence, NW architecture that offers a larger degree of freedom toward biaxial strain relaxation compared to planar layers may solve the lattice mismatch issue. So far, (In,Ga)N NWs with In composition spanning the entire range from GaN to InN without any phase separation have indeed been demonstrated by halide chemical vapor deposition (H-CVD) (Kuykendall et al., 2007). These NWs were grown in a self-induced approach and elongated toward [002]. (In,Ga)N NWs have also been fabricated by

MOCVD either on *R*-plane sapphire, and in this case they exhibited the *N*-plane and two semipolar {1-101} side facets (Kuo, Oh, & Ku, 2013), or on Si with Au-catalyst yielding NW axis elongation parallel to the *M*-direction (Liu et al., 2014). By MBE, InN (Calarco, 2012; Grandal et al., 2007; Nishikawa et al., 2007) and (In,Ga)N (Laskar et al., 2013; Tabata et al., 2012) NWs with growth axis parallel to *C*-[0001] and *M*-{10-10} facets can be obtained by a self-induced approach on Si(111) as well. In addition, the growth of *A*-{1-210} InN NWs by MBE on *A*-{1-210} GaN was also achieved, and in this case the NWs exhibited *M*- and *C*- lateral facets. Another potential of the NW architecture lies in the choice of direction for the heterostructure fabrication. Radial (Ha, Kim, & Choi, 2013; Le Boulbar et al., 2013; Limbach et al., 2011; Qian et al., 2004), axial (In,Ga)N–GaN (Albert et al., 2012; Kehagias et al., 2013; Roshko et al., 2014), or (In,Ga)N–InN (Cui et al., 2012), or a combination of both heterostructures (Tourbot et al., 2012) (quantum dots in a wire) have thus been grown. The careful assessment by conventional methods such as X-ray diffraction, PL, Raman spectroscopy, and TEM (Wölz et al., 2011, 2012) of MBE grown ensemble of axial heterostructures revealed strong fluctuations in composition and size of the (In,Ga)N QWs and the presence of an additional mechanism for carrier localization compared to planar heterostructures, namely band bending (Calarco, 2012; Wölz et al., 2012) resulting from lateral inhomogeneous strain. This effect yields an increase of the photoluminescence emission with the In content (Murotani et al., 2013) via limitation of nonradiative recombination at surface defect states. Taking advantage of the three heterostructure geometries, NW-based devices have been successfully demonstrated. Besides the realization of blue (Qian et al., 2004), green (Kishino & Yamano, 2014; Limbach et al., 2012), and near-IR (Kishino, Kamimura, & Kamiyama, 2012), color-tunable (Qian et al., 2005) and white LEDs grown on Si(111) (Lin et al., 2010) and on Si(001) (Guo et al., 2010), single NW LED with graphene *p*-contact (Tchernycheva et al., 2014), monolithic integration of green and amber LEDs (Kishino, Nagashima, & Yamano, 2013), single photon emitters (Deshpande, Das et al., 2013; Deshpande, Heo et al., 2013), optochemical sensors of oxidizing gases (Maier et al., 2014), water splitting photocatalyzers (Kamimura et al., 2013; Kibria et al., 2013), solar cells (Howell et al., 2013; Nguyen, Li, & Mi, 2012), or lasers (Arafin, Liu, & Mi, 2013; Frost et al., 2014) are the most impressive ones. However, achieving homogeneous high carrier injection in optoelectronic devices is still a big challenge (Bavencove et al., 2011; Limbach et al., 2012; Zhang et al., 2014) and is impeded by the enhanced surface recombination. Passivation of the NW surface is thus a requirement in order to substantially improve the carrier injection efficiency (Zhang et al., 2014).

4.5 (Al,Ga)N alloy and heterostructure nanowires

The growth of homogeneous (Al,Ga)N NWs is not an easy task because it is essentially ruled by kinetics aspects, that is the limited surface diffusion of Al adatoms compared to the one of Ga atoms (Pierret, Bougerol, Murcia-Mascaros et al., 2013; Su et al., 2005). Thus, though attempts to grow self-induced (Al,Ga)N NWs over the whole compositional range by MBE (Bertness et al., 2006; Park et al., 2006; Pierret,

Bougerol, Gayral et al., 2013; Pierret, Bougerol, Murcia-Mascaros et al., 2013) were made, strong Al composition fluctuation was observed along the NW axis (Pierret, Bougerol, Gayral et al., 2013; Pierret, Bougerol, Murcia-Mascaros et al., 2013), even yielding to spontaneously formed (Al,Ga)N core–shell structures with a Ga-rich core and an Al-rich shell (Allah et al., 2012). Similarly, the growth by MOCVD of (Al,Ga)N NWs was reported to result in Al(Ga)N/GaN radial heterostructures with GaN core (Su et al., 2005). However, a recent two-growth temperature step method (Carnevale et al., 2011) was proven efficient in forming either vertical or coaxial AlN–GaN sharp superlattices by adjusting adatom mobility. Both radial (Jacopin et al., 2012) and axial (Jacopin et al., 2013; Ristić et al., 2003) intentionally grown heterostructures have been fabricated not only to be implemented in the active region of optoelectronic applications but also to access essential properties of the NW architecture. For self-induced growth of GaN NWs in MBE, (Al,Ga)N layers have been employed as markers in order to precisely study the NW growth kinetics and compare the growth rate of the axial and radial facets (Calarco et al., 2007; Songmuang, Landré, & Daudin, 2007; Tchernycheva et al., 2008). Attempts to conduct a similar study using a Ni-catalyst approach also by MBE resulted, however, in random heterostructures within the NWs (Lari et al., 2011). The pioneering fabrication of GaN–(Al,Ga)N nanocavities with AlN–GaN Bragg reflectors by MBE from the Calleja group allowed probing the quantum confinement effects on the PL emission. These were found to depend on the quantum disk thickness and the inhomogeneous strain distribution within the latter (Ristić et al., 2005). Since then, similar studies have been carried out with the fabrication of GaN NWs containing (Al,Ga)N–GaN single-quantum disks of various thicknesses to study the dependence of the micro-PL transition energy on disk thickness and diameter. A 3D-model of the quantum confinement developed to take into account the residual doping, the strain, and the polarization revealed in addition the influence of the lateral (Al,Ga)N shell thickness on emission energy (Jacopin et al., 2013; Rigutti, Teubert et al., 2010). AlN–GaN superlattices with various well thicknesses were also studied to determine the strength of the intrinsic electric field (Buchheim et al., 2007). Comparison of GaN NW with or without (Al,Ga)N shell allowed identification of a GaN surface state at $E_v + 2.6$ eV by deep level optical spectroscopy and revealed the suitability of the (Al,Ga)N shell for surface passivation (Armstrong et al., 2010). To further improve LED performances, designs including p-doped (Al,Ga)N electron blocking layer were shown to enable the effective control of electron overflow in phosphor-free NW white LEDs (Nguyen et al., 2012). The results of these first studies have aided the realization of many optoelectronic devices such as resonant tunneling diodes (Carnevale, Marginean et al., 2012), single GaN/AlN multiquantum disk NW photodetectors in the UV range (Rigutti, Tchernycheva et al., 2010), polarization-induced deep UV LEDs based on graded NW (Al,Ga)N (Carnevale et al., 2013) emitting from 3.4 to 4.7 eV (Carnevale, Kent et al., 2012), UV LED based on GaN–(Al,Ga)N multiquantum disks emitting at 354 nm on Si(111) (Sekiguchi, Kato et al., 2008), and on n-ZnO/p–(Al,Ga)N heterojunction emitting at 394 nm (Tang, Li, & Zhou, 2013), self-assembled (Al,Ga)N polarization-induced NW LEDs with Gd-doped AlN active region emitting at 318 nm (Kent, Carnevale, & Myers, 2013), quantum wire UV laser (Choi et al., 2003), optochemical

transducers (Teubert et al., 2011), room temperature NW polariton laser (Das et al., 2013), GaN/AlN/(Al,Ga)N metal-insulator semiconductor field effect transistor (Vandenbrouck et al., 2009), GaN/AlN/(Al,Ga)N radial NW high electron mobility transistors (Li et al., 2006), or undoped (Al,Ga)N shell/GaN core NW transistor with *p*-type conductivity (Mastro et al., 2010). Thus, the NW geometry is extremely versatile for combining very different materials, and their potential for new technologies in electronics and photonics should enable their integration into real world devices in a near future.

4.6 Conclusions

In this chapter, the structural and optical properties of GaN, (In,Ga)N, and (Al,Ga)N NWs have been discussed in detail by reviewing the most prominent growth techniques such as MOCVD and PA-MBE. In this respect, catalyst-induced growth by VLS mechanism and the self-assembled growth of NWs were compared. It was found that the NW radius and the formation of extended defects were affected by the presence of a catalyst particle. On the other hand, self-assembled NWs showed a defect-free single-crystalline nature. The density of GaN NWs grown by PA-MBE and their corresponding optical quality were influenced by the growth conditions such as substrate temperature and III/V ratio. GaN microcrystals born from GaN NWs have shown excellent optical quality, which makes them a potential candidate for the integration of efficient (In,Ga)N μ -LEDs. SAG of GaN NWs has been reviewed and different techniques to control the size and position of the NWs have been compared. The challenges of (In,Ga)N and (Al,Ga)N NW growth have been discussed. In particular, the compositional variation and phase separation problems related to the differences in growth temperatures have been addressed. Despite the challenges in the growth of GaN NWs alloyed with In and Al, the first successful devices have been already demonstrated. Further investigations using these material systems have the potential to enable them to be used in future production devices.

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Part Two

Characterizing the properties of semiconductor nanowires

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Self-assembly and organization of nanowires

5

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5.1 Introduction

The past decades have witnessed the rapid development of one-dimensional (1D) nanostructures such as nanowires (NWs), nanorods, nanobelts, and nanotubes, which have become the focus of intensive research owing to their unique applications in mesoscopic physics and powerful nanoscale functional devices (Dekker, 1999; Hu, Odom, & Lieber, 1999; Law, Goldberger, & Yang, 2004; Lieber, 2003; Li, Qian, Xiang, & Lieber, 2006; Xia et al., 2003). 1D nanostructures represent an important class of material platforms to investigate the dependence of many chemical and physical properties on the dimensionality and size reduction (or quantum confinement) (Hu, Ouyang, Yang, & Lieber, 1999; Sirbulu, Law, Yan, & Yang, 2005; Wang, Chen, Lin, Fang, & Lieber, 2005; Yu et al., 2000). They are also expected to play important roles as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions (Messer, Song, & Yang, 2000; Tian et al., 2007; Yan et al., 2001). Although 1D nanostructures have been successfully explored as functional nanodevices, often at a single device level, such as field effect transistors (Tans, Verschueren, & Dekker, 1998), photo-detectors (Kind, Yan, Messer, Law, & Yang, 2002), and chemical/biological sensors (Cui, Wei, Park, & Lieber, 2001), using a number of advanced nanolithographic techniques, such as electron-beam or focused-ion-beam (FIB) writing (Kempa et al., 2012; Moutanabbir et al., 2013), X-ray, or extreme-UV lithography (Morales & Lieber, 1998), critical challenges still remain in further development of practical routes to effectively integrate large quantities of 1D nanostructures from chemically distinct materials.

To construct NW-based functional nanosystems and realize their promising applications, considerable effort has been placed on developing methods of assembly of NWs. For instance, assembly of the NWs on specific substrates toward potential electronic/optoelectronic applications usually requires two steps: the first step is the aligned growth of NWs, and the second step is the transfer of the aligned NWs to the target substrates (Yu & Lieber, 2010). Although patterned NWs and devices can be fabricated by conventional lithography technologies taking advantage of the precision and repeatability of the top-down fabrication, it is becoming obvious that both physical and economic factors of current lithography technologies will limit further advances of the integrated circuit industry. In contrast to top-down fabrication approaches, NWs can be grown via bottom-up approaches such as solution growth

(Holmes, Johnston, Doty, & Korgel, 2000; Vayssieres, 2003; Xia et al., 2003), vapor–liquid–solid method (Gudiksen, Lauhon, Wang, Smith, & Lieber, 2002; Gudiksen & Lieber, 2000; Wu & Yang, 2001; Yang et al., 2002), and electrochemical deposition (Lee, Lee, & Leez, 2010; Mallet et al., 2008; Ponroucha et al., 2010) into nanoporous templates at a relatively low cost. However, the as-grown NWs often have random alignment and orientation. These randomly aligned NWs have to be assembled and organized into integrated arrays for subsequent device building in a highly controllable manner. These assembly approaches must be devised to hierarchically assemble NWs on multiple length scales and to make interconnects between nano-, micro-, and macroscopic worlds.

This chapter mainly discusses the general assembly strategies that exploit different interactions and/or directed forces to drive the rational organization of semiconductor NWs into well-ordered arrays with controlled orientation, alignment density, and spatial position. We aim to present recent progress toward NW device assembly techniques, including Langmuir–Blodgett (LB) assembly (Cao et al., 2013; Li et al., 2007; Tao et al., 2003; Whang, Jin, & Lieber, 2003; Whang, Jin, Wu, & Lieber, 2003), optical trapping method (Agarwal et al., 2005; Pauzauskie et al., 2006), contact printing (Fan et al., 2008; Javey, Nam, Friedman, Yan, & Lieber, 2007; Yao, Yan, & Lieber, 2013; Yerushalmi, Jacobson, Ho, Fan, & Javey, 2007), electric/magnetic field-directed assembly (Duan, Huang, Cui, Wang, & Lieber, 2001; Hangarter & Myung, 2005; Smith et al., 2000; Tanase et al., 2002), microfluidic assembly (Huang, Duan, Wei, & Lieber, 2001), chemically driven assembly (Keren, Berman, Buchstab, Sivan, & Braun, 2003; Lee et al., 2006; Rao, Huang, Setyawan, & Hong, 2003), and blown bubble film (BBF) technique (Yu, Cao, & Lieber, 2007; Yu, Li, Lieber, & Cao, 2008). This chapter will also exemplify the ability to organize different types of functional semiconductor NWs onto different substrates, which are ultimately necessary for device fabrication of high performance, flexible electronics, sensors, photovoltaics, and bioelectronic interfaces.

5.2 Langmuir–Blodgett technique

Scalable and controlled assembly of the NWs is of high importance and necessity to utilize the great potential of NWs for a broad range of technological applications. Considerable efforts have been devoted to developing methods to assemble NWs into desired organization with controlled density, position, and orientation that might ultimately lead to integrated systems. For example, there have been studies that offer centimeter-scale assembly of NWs using the LB technique, much beyond those individual or small numbers of NW-based devices prepared by random deposition.

Whang et al. reported a general and efficient solution-based LB technique for controlling the organization and hierarchy of NW structures over large areas (Whang, Jin, Wu et al., 2003). The LB technique was successfully applied to realize the well-aligned NWs with controlled spacing from nanometer to micrometer scale and transfer to

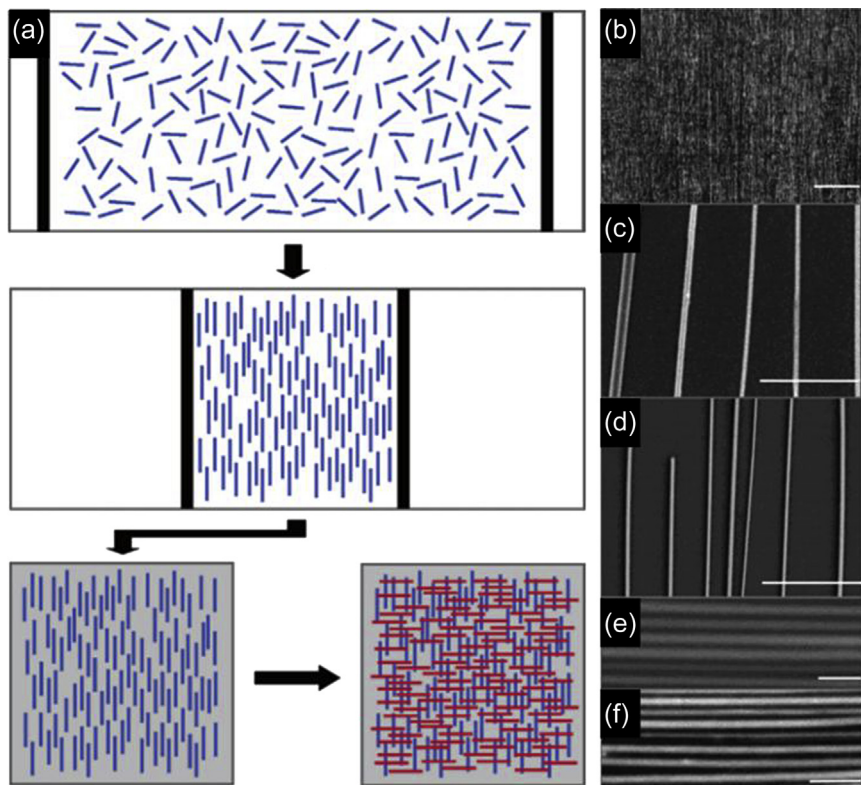


Figure 5.1 Fabrication processes and the demonstration of the controlled spacing and orientation of semiconductor NW arrays. (a) Schematic steps of the LB technique. (b) Large-area SEM image of parallel NWs deposited uniformly on the substrate. Scale bar, 100 μm . (c, d) SEM images of aligned parallel NWs transferred to substrates at different stages of LB compression. Scale bars, 1 μm . (e, f) SEM images of high-density parallel NW arrays on the substrates. Scale bars, 200 nm.

Reproduced with permission from Whang, Jin, Wu et al. (2003), Copyright 2003, American Chemical Society.

planar substrates via a layer-by-layer (LBL) process to form parallel and crossed NW structures (Figure 5.1). The assembled NW structures were subsequently patterned into repeating arrays of controlled dimensions and pitch using photolithography to yield hierarchical structures across multiple-length scales from the nanometer to centimeter ordering. This work demonstrated that the LB technique is a promising approach for large-scale assembly of virtually any NW material into highly integrated and hierarchically organized nanodevices catering for a broad range of functional nanosystems (Whang, Jin, & Lieber, 2003).

The LB technique is commonly applied to transfer the monolayers of organic materials onto a solid substrate to form extremely thin film (LB film) with a high degree of structure order, and it has been found to be a powerful approach to achieve NW

assembly on larger scales with precise NW spacing down to the nanometer level and controlled densities (Yang, 2003; Figure 5.1(a)). In the NW assembly process, a surfactant-wrapped NW monolayer is initially formed on a liquid surface in an LB trough. The surfactants wrap around the NWs' surface and enable the wires dispersed in a fluidic medium and floated at the fluid–air interface. The monolayer is then compressed using an LB trough barrier under an appropriate level of compression. The NWs are close packed as parallel arrays with their longitudinal axes aligned perpendicular to the compression direction to minimize the surface energy of the liquid, and the monolayer is then transferred onto a substrate through vertical-dipping or horizontal-lifting techniques. The spacing between the parallel NWs can be well controlled by adjusting the lifting speed and the compression pressure, as shown in Figure 5.1(b)–(f). Parallel and crossed NW structures with high density have been assembled by single and sequential transfer steps over centimeter-length scales; moreover, functional devices based on such NW LB films have been fabricated, although it is unclear whether the centimeter-square arrays of NWs can be scaled further to larger areas with high efficiency and transferred to nonrigid or curved surfaces, such as flexible plastic substrates.

Tao et al. used the LB technique to assemble aligned monolayers of silver NWs that are ~ 50 nm in diameter and $2\text{--}3\text{ }\mu\text{m}$ in length over areas as large as 20 cm^2 (Tao et al., 2003). The SEM images of the resulting Ag NW arrays on a Si wafer show that the assembled NWs are close packed and are aligned parallel to each other

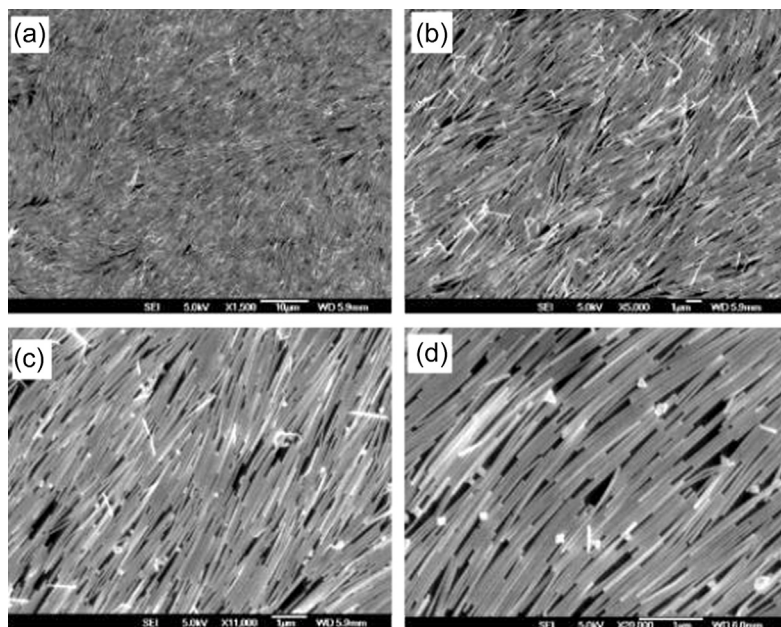


Figure 5.2 SEM images of the silver nanowire monolayer deposited on a silicon wafer. Reproduced with permission from Tao et al. (2003), Copyright 2003, American Chemical Society.

(Figure 5.2). The Ag NW monolayers serve as excellent substrates for surface-enhanced Raman spectroscopy with large electromagnetic field enhancement factors.

Similarly, the Ag NWs were first dispersed in a fluidic medium and then deposited onto a water surface in the LB trough. It is important to note that the displacement of the PVP capping agents with thiol ligands is critical in rendering the NW surface hydrophobic as well as preventing NW aggregation. The assembly process is a microscopic version of “logs on a river.” The monolayer of the aligned NWs is then transferred onto a substrate. Most importantly, the compressed Ag NW monolayer exhibits remarkable alignment parallel to the trough barrier. Figure 5.2 shows SEM images of the monolayer transferred onto a silicon wafer. The NWs are aligned side by side over large areas, resembling a nematic two-dimensional ordering of a liquid crystal. These large-scale directional-ordered NW arrays offer promising integrity for fabricating the large-scale organized nanodevices for integrated nanosystems.

5.3 Optical trapping method

Optical trapping has the advantage of being able to assemble semiconductor NWs into complex heterostructures with high spatial and angular precision in three-dimensional (3D) orientations. It also shows the capability to act in situ in closed aqueous chambers, potential applicability to a wide range of materials, and the tunability of their intensity, wavelength, and polarization by applied lasers, modulators, and holographic optical elements.

Yang et al. demonstrated the trapping of NWs made from different materials in a single-beam optical-tweezers system (Figure 5.3; Pauzauskie et al., 2006). GaN, SnO₂, ZnO, and Si NWs were successfully trapped in their experiments; only about 6.5% of 200 SnO₂ nanoribbons showed unexpected periodic oscillations. The NWs were picked up by aiming the laser trap at one of the NW's ends and then translating the trap along the wire, simultaneously raising the trap. Once the NWs were trapped stably, one end of the wires was in the laser focus and the rest of the wire was parallel to the optical axis, thus being confined in all three dimensions.

The trapped NWs can be further translated by performing either a home-built translation stage for long distances or a three-axis piezostage for fine control. Velocities of 10 $\mu\text{m/s}$ could be achieved in three axes. It is also possible to fuse two wires by a focused infrared beam in the optical trap system. By applying laser irradiation with higher power than that for trapping on the crossing point of two wires for 5 s, two wires stopped moving and could not be pulled apart. It is possible that local temperatures at the junction can approach the melting point of NWs and thus the wires were fused.

Capable of manipulating, positioning, and fusing NWs provided by the laser nanowire assembly (LNA) method, three GaN and two SnO₂ NWs were assembled to achieve an approximately 300-nm-tall cabin consisting of passive waveguides (SnO₂ nanoribbons) and subwavelength ultraviolet nanolasers (GaN NWs) and with six optically fused junctions. The application of LNA in a biological field was also demonstrated. Optically trapped NWs can be positioned with respect to living cells. One end of GaN NW could be placed against the cell membrane or pushed into the

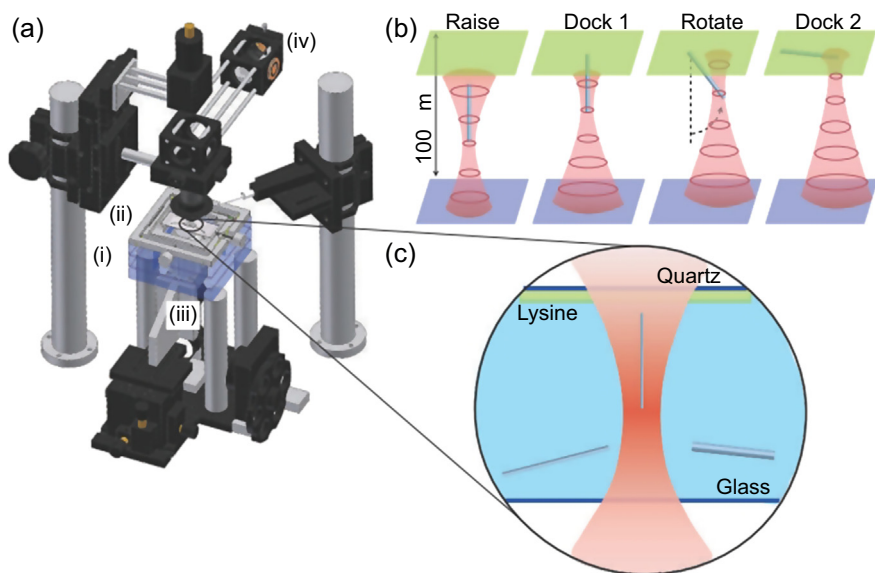


Figure 5.3 Fabrication processes of the optical trapping method for NW assembly. (a) Schematic of the optical trapping instrument. (b) Schematic four-step NW positioning procedure. (c) Schematic of the experimental chamber cross-section. Reproduced with permission from [Pauzauskie et al. \(2006\)](#), Copyright 2006, Nature Publishing Group.

cell. Then it was possible to image live cells and tissues by scanning the end of GaN wire.

It is worth noting that the positioning accuracy of LNA is limited significantly by Brownian fluctuations, but it is still significantly better than those achievable with microfluidic channels or the LB technique.

Lieber et al. developed a similar method using holographic optical traps (HOTs) as a general approach for parallel manipulation and assembly of NWs ([Figure 5.4](#); [Agarwal et al., 2005](#)). The HOT technique can create hundreds of independently controlled optical traps that can manipulate objects in 3D. CdS NWs with cross-sections were isolated, translated, rotated, and deposited onto a substrate with the HOT technique. The NWs were synthesized and then suspended in ethanol. NW samples were manipulated and observed on the stage of a Nikon TE-2000U microscope with a $100\times$ NA 1.4 Plan Apo oil-immersion objective. The lens is used to collect images and also to focus light from a Nd:YVO₄ laser into optical traps. The HOT technique was utilized to create a larger number of optical traps.

To exert more force on the NWs while minimizing the radiative damage, large numbers of HOTs were projected along each NW. The trap array maintains the NW's orientation and can translate the wires. As few as two traps can capture and

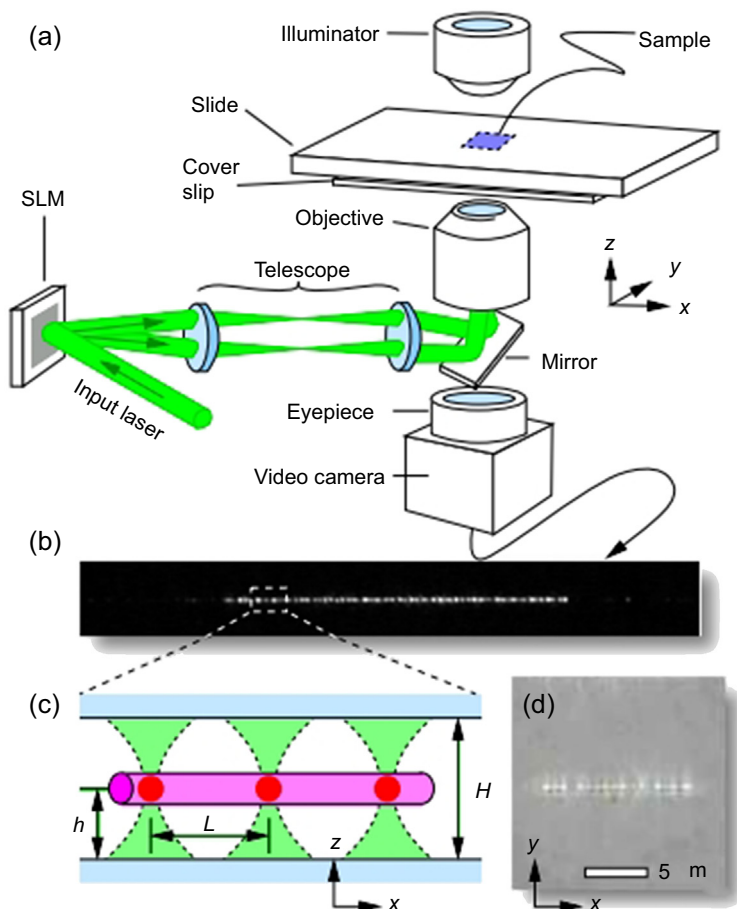


Figure 5.4 Fabrication processes of the HOT method for NW assembly. (a) Before being relayed to the input pupil of a high-numerical-aperture objective lens, the light is imprinted with a computer-generated hologram. (b) The modulator focuses the light into an array of optical traps. (c) An individual semiconductor NW can be localized by multiple optical traps. (d) Intersection with the wire typically is visualized by intense laser-induced fluorescence. Reproduced with permission from [Agarwal et al. \(2005\)](#), Copyright 2005, Optical Society of America.

translate an NW. Additionally, the HOT method can also manipulate multiple NWs simultaneously and independently in complex ways.

Other modes of optical manipulation that could be important for assembling complex structures were investigated on HOT arrays. First, trapped NWs can be translated along the optical axis to the surface of a substrate. Second, NWs can be cut by focusing optical traps at higher powers. This mode provides new opportunities for creating junctions. For example, a T-junction could be irreversibly fused by applying a high-power pulse.

5.4 Contact printing method

Rational integration of NWs into functional circuits requires them to be assembled with controlled orientation and density at spatially defined locations on the device substrate. Previously, we discussed one of the solution-phase methods for assembling aligned and controlled density arrays of NWs on substrates, the LB technique. While success has been achieved with these approaches for assembling single-layer arrays of functional NW devices using 20–40-nm-diameter NWs, these methods have been less successful with small (<15 nm)-diameter NWs. To overcome this limitation, a new dry deposition strategy that involves the shear force has been developed to enable oriented and patterned assembly of small-diameter NWs with controlled density and alignment on substrates, from Si growth wafer to different substrates.

Javey et al. reported a dry deposition strategy to fabricate the highly oriented and patterned NW thin film for 3D multifunctional electronics (Javey et al., 2007). The overall process for the contact printing method involves two major processes: (1) optimizing the oriented growth of designed NWs by nanocluster directed growth, and (2) patterned transferring of the NWs directly from an NW growth substrate to a second device substrate via contact printing, as illustrated in Figure 5.5(a). Specifically, a photolithography-patterned substrate is first firmly attached to a benchtop, and the NW growth substrate is placed upside down on top of the patterned substrate such that the NWs are in contact with the device substrate. A gentle manual pressure is then applied from the top followed by sliding the growth substrate. Finally, the growth substrate is removed. During the assembly process, a shear force is created by the motion of a fluid or solid object against a second fluid or solid object. This motion can be achieved either by the wetting/dewetting of surfaces or the mechanical movement of two surfaces in opposite directions. In either case, a force is generated parallel to the direction of movement. This force can be used to redirect the orientation of the NWs that are either suspended in a solution or fixed to a substrate. The new orientation of the NWs will be parallel to the direction of the shear force.

Furthermore, devices and circuits can be fabricated on the printed arrays of NWs using conventional top-down lithography and metallization processes (Yerushalmi et al., 2007). To elaborate a 3D structure, the NW printing and device fabrication steps are iterated multiple times, along with the deposition of an intervening insulating SiO₂ buffer layer, in order to obtain vertically stacked electronic layers (Figure 5.5(b)). This process is general for the wide range of reported NW materials and device designs; moreover, the simplicity and the low processing temperature requirement of the method make it ideal for achieving high-performance 3D-integrated circuitry with different functionalities in distinct layers.

5.5 Electric field-assisted assembly

Metallic NWs in a suspension could be precisely aligned by utilizing alternating electric fields between two lithographically defined metal pads. Mayer et al. demonstrated the alignment of Au NWs ranging from 70 to 350 nm in diameter by this technique

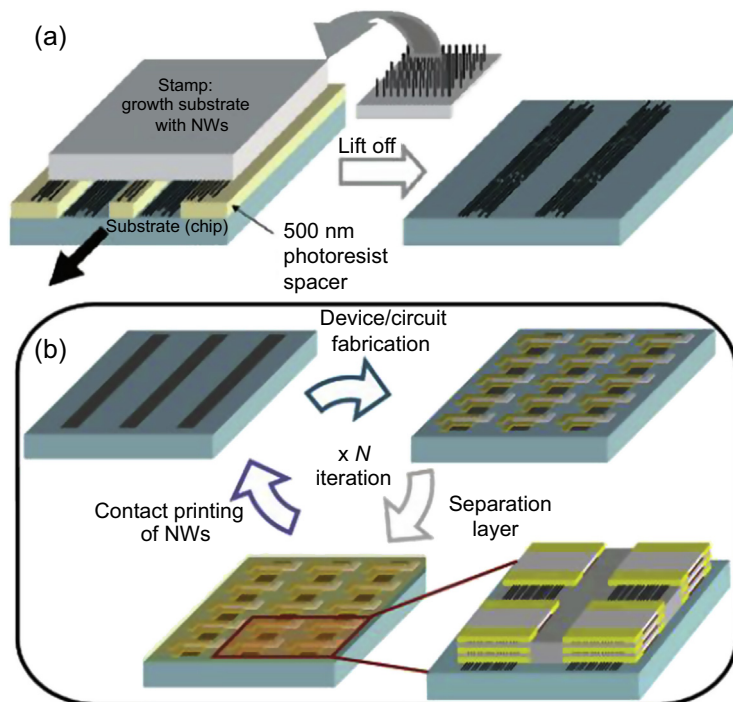


Figure 5.5 Schematic illustrations of contact printing. (a) Contact printing of NWs from the growth substrate to a prepatterned substrate. In general, NWs are grown with random orientation and become aligned by shear forces during the printing process. (b) The 3D NW circuit is fabricated by the iteration of the contact printing, device fabrication, and separation layer deposition steps N times.

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(Smith et al., 2000). The electrically isolated electrodes used to assemble the NWs are shown in Figure 5.6. The metal electrodes consist of an interdigitated finger pattern defined by a metal liftoff of 50 nm Ti/150 nm Au on a silicon substrate. The finger width and separation was 3 μm and 5 μm , respectively.

The NWs dispersed in the dilute suspension could be polarized readily in the alternating electric field with voltages ranging from 5 to 70 V due to charge separation at the surface of the NWs. The metallic NWs will experience a dielectrophoretic force, which produces net movement in the direction of increasing field strength. The electric field strength between electrodes and NW tips increases proportionally to the inverse of the distance from the electrodes as the NWs approach the electrodes with spacing approximately equal to the length of the NWs. The large near-field force results in alignment of the NWs between two electrode fingers. The strength of the forces exerted on the NWs is related to voltage, and the alignment of NWs was also frequency dependent. The alignment time could be reduced by increasing frequency. At low frequencies, the charge separation on the NWs was shielded by the polar molecules in

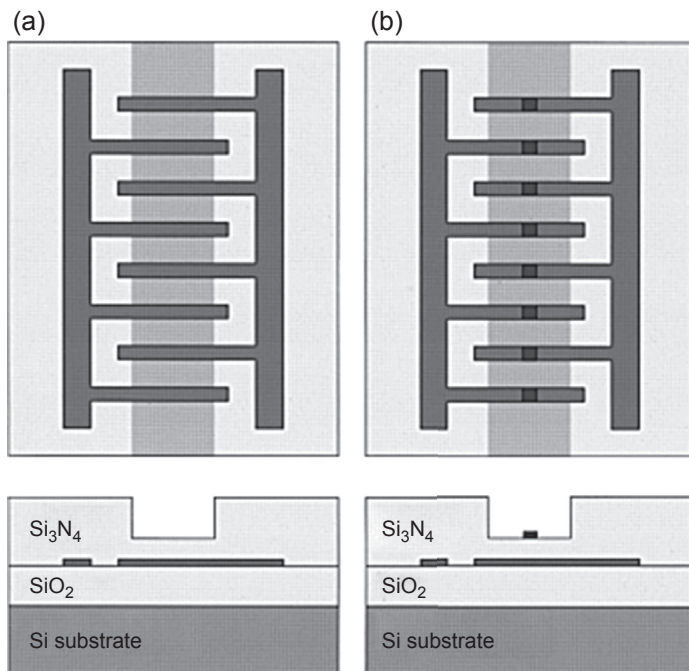


Figure 5.6 Top and cross-sectional views of the electrodes used in field-assisted assembly of nanowires. (a) Ti/Au electrode fingers are separated by 5 μm . (b) The same electrode structure with top electrodes added to improve the alignment precision.

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dielectric medium, leading to low alignment forces. As the frequency increases, the polar molecules with long relaxation times cannot reorient in a rapidly changing field, thus enhancing the alignment forces.

Semiconductor NWs could also be assembled by applying an electric field. In addition, a higher level of complexity in which an individual NW is aligned and positioned into parallel and crossed arrays has been demonstrated by Lieber et al. ([Figure 5.7](#); [Duan et al., 2001](#)). Parallel electrodes could align a large number of NWs along the direction of the electric field. Such assembly of NWs between an array of electrodes shows that individual wires can be positioned to bridge pairs of opposed electrodes and form a parallel ordered array. Furthermore, the alignment could be conducted in an LBL fashion to produce crossed NW junctions. Good directional and spatial control of alignment of NWs could be achieved by electric field-assisted assembly technique.

5.6 Magnetic field-assisted assembly

Magnetic NWs suspended in liquid could be assembled and manipulated onto substrates using external and locally applied magnetic fields. Tanase et al. demonstrated

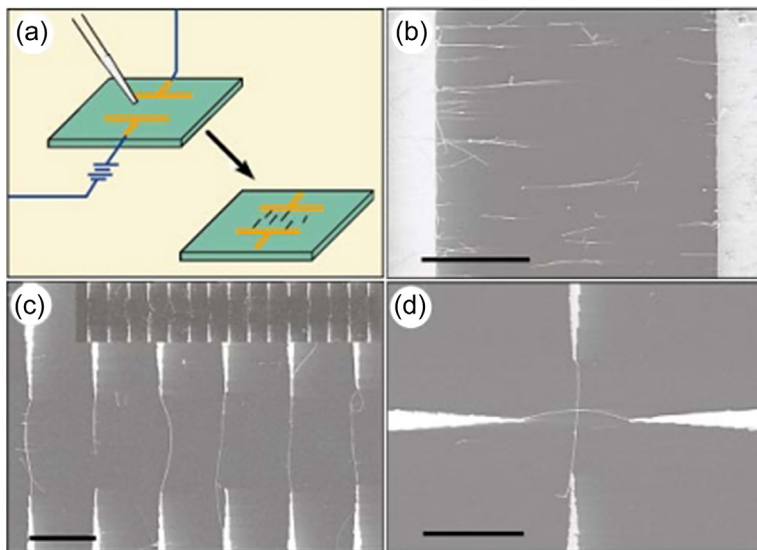


Figure 5.7 Electric field-assisted assembly of nanowires. (a) The electrodes are biased at 50–100 V after nanowire solution is deposited on the substrate. (b) Parallel NW array assembled between two parallel electrodes at a bias voltage of 100 V. (c) Spatially positioned parallel array of nanowires between electrodes with a bias of 80 V. (d) Crossed NW junction assembled by an LBL alignment with electric field applied in orthogonal directions in two steps. Reproduced with permission from [Duan et al. \(2001\)](#), Copyright 2001, Nature Publishing Group.

that Ni NWs with an average diameter of 350 nm and a length of 12 μm suspended in water could self-assemble when settled onto flat, glass substrates ([Figure 5.8](#); [Tanase et al., 2002](#)). The magnetic NWs could interact with each other through dipolar forces and tend to aggregate, however, usually in random orientation. Controlled assembly could be achieved by applying a small external field ($H < 10\text{G}$), which can help suppress the tendency toward random aggregation and result in the formation of head-to-tail NW chains (extended over several hundred micrometers). The morphology of the chains is dominated by the strength of the external field. At higher fields the chains become straighter and the tendency to form multiple branches is eliminated. The dynamics of chain formation could be described quantitatively in terms of magnetic forces and fluid drag at low Reynolds number.

NWs with capped magnetic ends can also be spatially manipulated and positioned on prefabricated ferromagnetic contacts taking advantage of magnetic interaction between contacts and NWs. Myung et al. demonstrated this alignment technique by utilizing NWs with magnetic ends or caps that facilitate a functional midsection ([Figure 5.9](#); [Hangarter & Myung, 2005](#)). A gold midsection was used in their experiments with Ni caps, but the midsection is interchangeable with a variety of materials including metals, metal oxides, alloys, semiconductors, and conductive polymers.

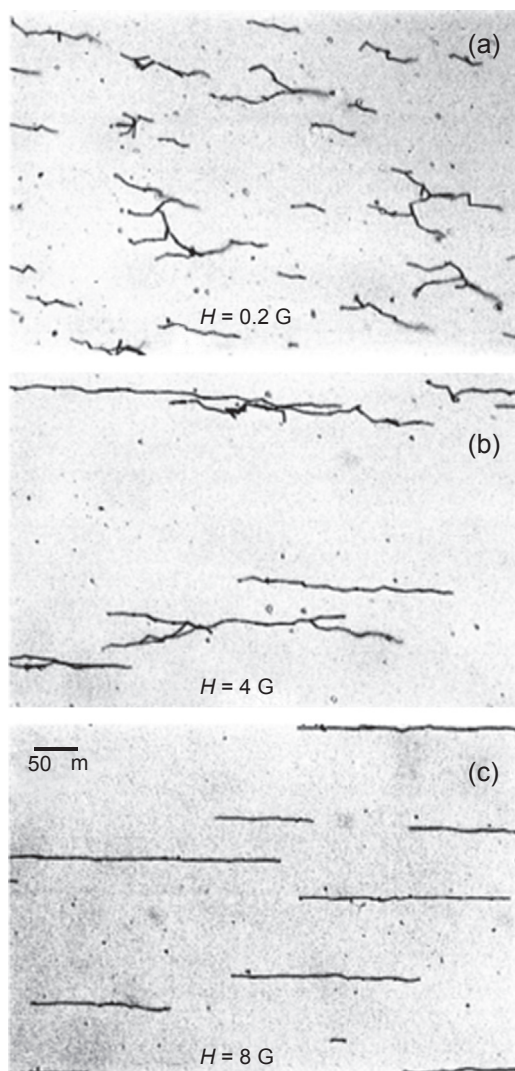


Figure 5.8 Optical micrographs of formation of Ni NW chains in external magnetic fields. Reproduced with permission from [Tanase et al. \(2002\)](#), Copyright 2002, American Institute of Physics.

Positioning of the NWs is dictated by the interactions between the ferromagnetic ends on the NW and the ferromagnetic contacts. The NW alignment maximizes the length of Ni ends adjacent to or between the ferromagnetic pads. High-density alignment of NWs is achieved by sequential alignments with a dilute NW suspension in fixed magnetic field and direction. This alignment technique also allows rotation of the substrate orientation with respect to the magnetic field to form more complex nanostructures. By

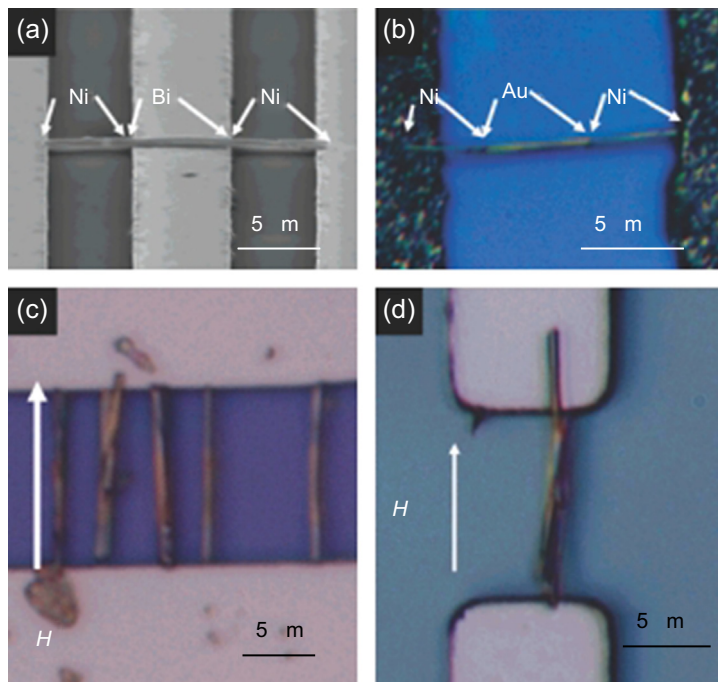


Figure 5.9 (a) A single Ni/Bi/Ni nanowire is aligned on nickel lines; (b) optical image of a single Ni/Au/Ni nanowire aligned between solder-plated nickel electrodes; (c) magnetic alignment for individual addressability with a single aligned Ni/Au/Ni nanowire; (d) high-density arrays achieved with multiple alignments of a dilute suspension.

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lithographically patterning the electrodes perpendicular to one another and rotating the magnetic field, a complete range of directions can be attained.

5.7 Microfluidic assembly

The hierarchical assembly of 1D NWs can also be achieved in fluid flows with controlled separation and spatial location, which was developed by Lieber et al. ([Figure 5.10](#); [Huang et al., 2001](#)). Except for parallel arrays of NWs, the method could also be applied to layer-by-layer assemble the crossed NW arrays with different flow directions for sequential steps.

The GaP, InP, and Si NWs were synthesized and then suspended in ethanol solution. The assembled NW arrays were achieved by passing suspensions of the NWs through fluidic channel structures formed between a poly(dimethylsiloxane) (PDMS) mold and a flat substrate. The NWs can be aligned along one direction, and the alignment has been found to extend up to millimeter-length scales.

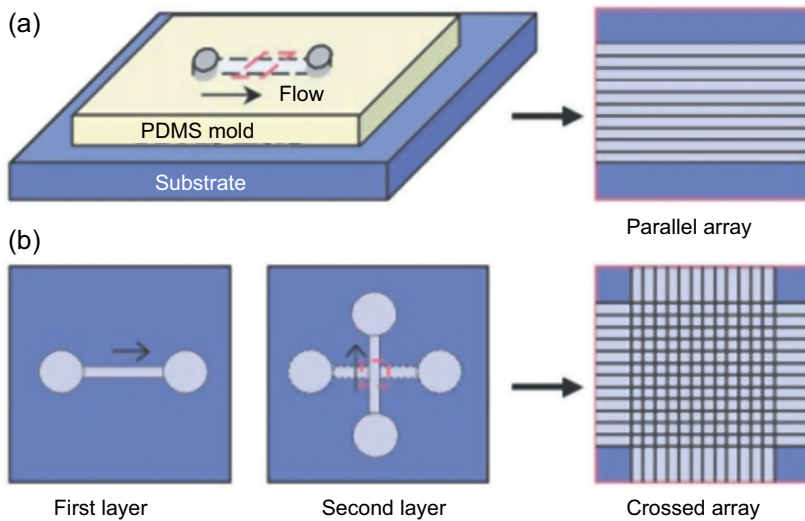


Figure 5.10 Schematic illustration of fluidic assembly. (a) Nanowires were assembled by flowing a suspension of nanowires with a controlled flow rate and duration inside the channel formed by contacting the PDMS mold with a flat substrate. Parallel arrays of nanowires could be observed in the flow direction on the substrate when the PDMS mold is removed. (b) Crossed NW arrays can be obtained by changing the flow direction sequentially in an LBL process. Reproduced with permission from [Huang et al. \(2001\)](#), Copyright 2001, American Association for the Advancement of Science.

The degree of alignment can be controlled by the flow rate. The width of the NW angular distribution with respect to the flow direction narrows with the increasing flow rates. This is caused by larger shear forces produced by higher flow rates. In addition, the average NW surface coverage can be controlled by the flow duration. Increased duration results in higher density of the NWs. The chemical states of substrate surfaces also play an important role in the NW assembly. The NWs deposit more rapidly on NH_2 -terminated substrates than on either methyl-modified substrates or bare silicon surfaces. The minimum separation of aligned NWs that can be achieved without wire–wire contacts depends on the lengths of the NWs used in assembly.

More complex crossed structures could be achieved by a fluidic method with an LBL process ([Figure 5.11](#)). For example, alternating the flow in orthogonal directions in a two-step assembly process yields crossbar structures, and a three-layer deposition sequence with 60° angles between three flow directions results in an equilateral triangle. More importantly, each layer in the LBL assembly process is independent of the others, providing the opportunities for heterojunction formation by changing the composition of the NW suspension used for each step.

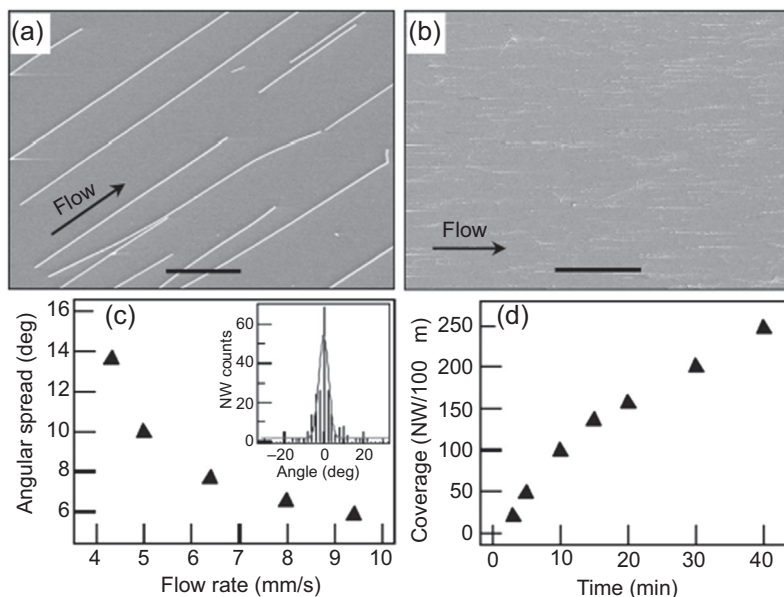


Figure 5.11 Parallel assembly of NW arrays. (a and b) SEM images of parallel arrays of InP NWs aligned by channel flow. The scale bars correspond to 2 and 50 μm in (a) and (b), respectively. (c) Nanowires' angular spread with respect to the flow direction versus flow rate. Each data point was obtained by statistical analysis of angular distribution of ~ 200 NWs. (d) The average density of nanowires with a flow rate of 6.40 mm/s versus flow time. Reproduced with permission from [Huang et al. \(2001\)](#), Copyright 2001, American Association for the Advancement of Science.

5.8 Chemically driven assembly

To overcome the lack of control over specificity and selectivity between NWs and target substrates, Hong et al. used organic molecules on a substrate to guide the assembly of single-walled carbon nanotubes (SWCNTs) in large scale ([Figure 5.12](#); [Rao et al., 2003](#)). First, they created distinct surface regions on the substrate; one was coated with polar chemical groups (such as amino or carboxyl) and the other was coated with nonpolar groups (such as methyl). Then the substrate was placed in a suspension of SWNTs and the nanotubes would be chemically attracted toward the polar regions and assembled to form predesigned structures.

The nanotubes were rotated by a lateral-directional force that originated from electrostatic interactions existing on SWCNTs near the boundary between the polar and nonpolar molecular regions. This force further confined the nanotubes to the inside of the polar region. The method could be scaled up for high-throughput assembly. Millions of SWCNT-based circuits over areas of about 1 cm ([Dekker, 1999](#)) could be assembled.

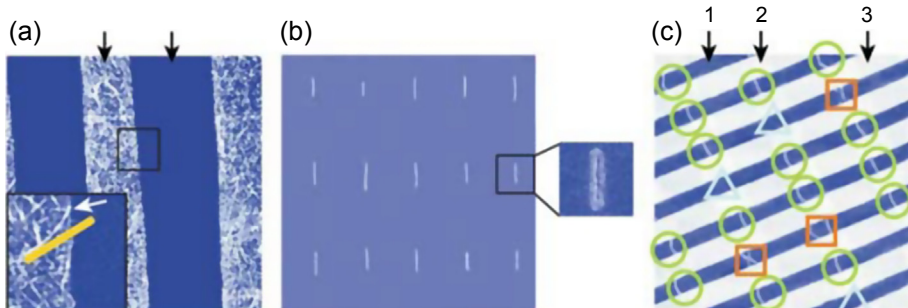


Figure 5.12 Large-scale self-assembly of SWCNTs. (a) Topography of SWCNTs near the boundary between polar (left arrow) and nonpolar (right arrow) areas on gold. (b) Topography of an array of individual SWCNTs covering about 1 cm^2 of gold surface. A single SWCNT (dark line) is shown in the friction-force image (inset). (c) An array of junctions with no SWNTs (triangles), one SWCNT (circles), or two SWCNTs (squares). Arrows 1, 2, and 3 indicate octadecyl-trichlorosilane on SiO_2 , 2-mercaptoimidazole on gold, and ODT on gold, respectively.

Reproduced with permission from [Rao et al. \(2003\)](#), Copyright 2003, Nature Publishing Group.

Similarly, chemically driven assembly could be applied to semiconductor NWs by proper modification of the surfaces of NWs. For example, Lee et al. ([Figure 5.13](#); [Lee et al., 2006](#)) used inert surface molecular patterns to guide the adsorption and alignment of NWs onto bare surface regions on the substrates. SWCNTs and V_2O_5 NWs were successfully assembled and aligned on various substrates, including Au, silica, glass, and Si.

The first step of this method is patterning of a methyl-terminated self-assembled monolayer (SAM) onto solid substrates, leaving other parts of the surface untreated. The methyl-terminated SAM patterns could prevent the adsorption of NWs and guide them to assemble onto bare surface regions. Subsequently, the patterned substrate was placed in the solution of NWs. Various factors, such as charges and van der Waals interactions, will affect the adsorption behavior. SWCNTs show strong affinity to most bare surfaces due to the natural polarization of pristine surfaces, and the affinity could be used to direct SWCNTs assembly. Electric potential could be applied to enhance NW adsorption. For example, as V_2O_5 NWs were negatively charged in aqueous solution, positive bias could be applied to substrate to further guide the assembly of V_2O_5 NWs. This method could be applied on various substrates and large-scale fabrication of NW-based devices could be achieved based on this method.

In addition to chemical molecules used for chemically driven assembly, biomolecules such as DNA can also be used to construct complex architectures from molecular building wires, meeting the needs for precise nanofabrication and mechanical manipulation. Braun et al. demonstrated the assembly of SWCNTs via a three-strand homologous recombination reaction between a long double-stranded DNA (dsDNA) molecule serving as a scaffold and a short single-stranded DNA (ssDNA)

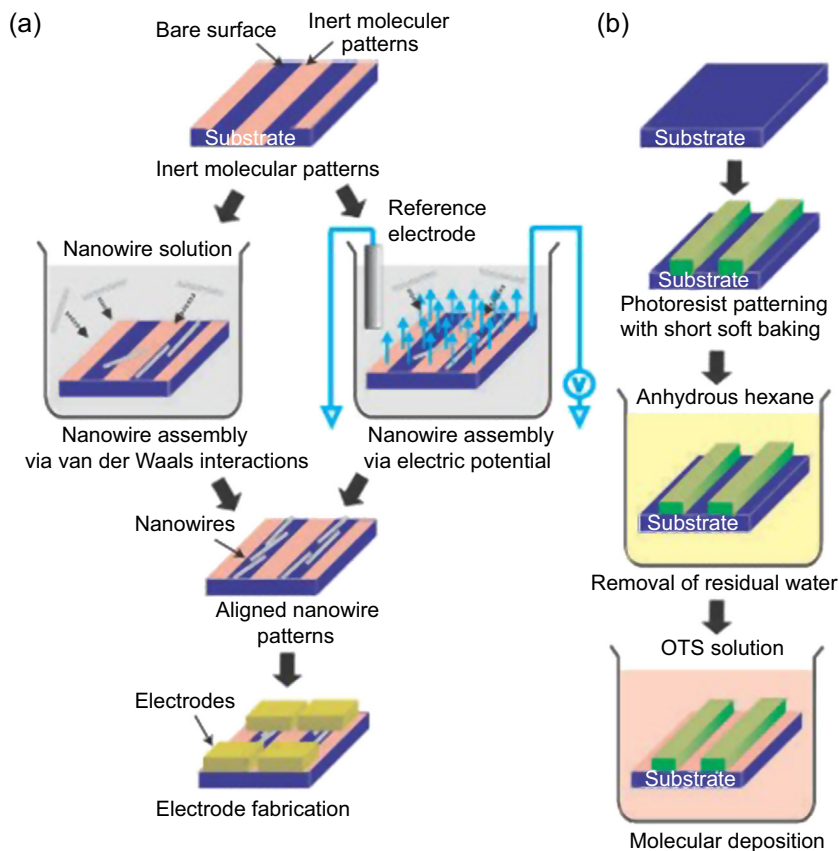


Figure 5.13 Schematic illustrations of the NW assembly and molecular-patterning method. (a) Molecular linker-free assembly method. The inert molecule treated part drives the adsorption and alignment of nanowires onto the bare surface regions on the substrate. (b) The patterning process of OTS SAM on solid substrates via photolithography. Reproduced with permission from Lee et al. (2006), Copyright 2006, Nature Publishing Group.

(Figure 5.14; Keren et al., 2003). The information encoded in DNA molecules guided the assembly. RecA proteins were first polymerized on the ssDNA to form nucleoprotein filaments. Then they were mixed with dsDNA molecules. A dsDNA molecule can be linked to the ssDNA according to the sequence homology. The RecA protein then guided the localization of an SWCNT at that address and protected the DNA segment. The SWCNT was first streptavidin functionalized and guided to the right location on the dsDNA using antibodies to the RecA and biotin–streptavidin-specific binding. The DNA/SWCNT assembly was then stretched on a silicon wafer. After the stretching, the DNA molecule was metallized, which can serve as the template for growth of gold wires.

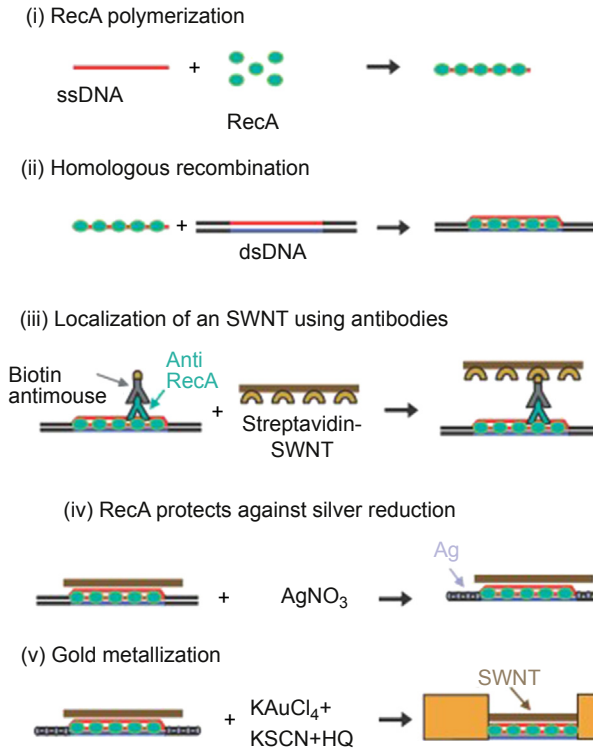


Figure 5.14 Schematic of assembly of a DNA-templated FET.

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The bio-driven method is a potential effective approach to align semiconductor NWs due to the ability of semiconductor NWs to be functionalized by various kinds of biomolecules ([Cui et al., 2001](#)).

5.9 Blown bubble film method

Scalable and controlled assembly of the NWs is of high importance, significance, and necessity in order to utilize the great potential of NWs in the field of electronic circuitry. However, there still remains a critical challenge in the very-large-scale assembly (meter scale) of NWs on both rigid and flexible substrates with controlled alignment and density.

Blown film extrusion is a potentially highly scalable process for fabricating well-ordered NW arrays on plastic films in large quantities, which involves extruding a molten polymer and inflating it to obtain a balloon, which can be collapsed and slit to form continuous flat films with widths exceeding 1 m at rates on the order of

500 kg/h. Yu et al. applied this BBF technique to the fabrication of NW/nanotube films where the location, density, and orientation of the NWs were controlled within the films (Yu et al., 2007). This BBF approach mainly involves three steps as is shown in Figure 5.15(a). First, a homogeneous, stable, and controlled concentration polymer suspension of different nanomaterials is prepared by chemically functionalizing the surface of the nanomaterials used. Second, bubble expansion of the polymer suspension is controlled using a circular die to form a bubble at controlled pressure P , and expansion rate via motor-directed force F . Finally, the BBFs are uniformly and conformally transferred to different substrate structures (Figure 5.15(b)–(d)).

The NWs within the film can be aligned along the shear force created by the expansion of the film. Over 85% of the NWs are aligned within $\pm 6^\circ$ along the upward expansion direction. For instance, Si NWs can be transferred conformally to single-crystal wafers up to 200 mm in diameter, flexible plastic sheets up to

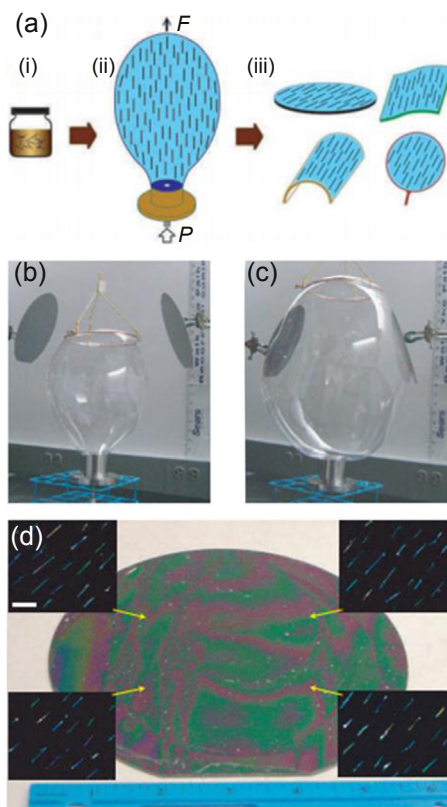


Figure 5.15 Blown bubble film (BBF) process. (a) Schematic illustration of BBF process. (b, c) Photographs of directed bubble expansion process at early and final stages, respectively. (d) Image of a 0.10 wt% Si NW-BBF transferred to a 150-mm Si wafer. Insets, dark-field optical images showing Si NWs in the film. Reproduced with permission from Yu et al. (2007), Copyright 2007, Nature Publishing Group.

225 × 300 mm, highly curved surfaces, and also suspended across open frames. The NW density within the film can be well tuned by controlling the concentration of the NWs in the polymer suspension (Figure 5.16(a)–(d)). The BBF approach was also used to transfer aligned NW and NT films to a broad range of substrates with different shapes and materials. For example, a Si NW-BBF was transferred to a half cylinder (Figure 5.16(e)), and subsequent dark-field optical images confirm that the NWs within the film are well aligned. NW- and NT-BBFs can be transferred to flexible plastic substrates that are subsequently bent into curved structures. In addition to planar and curved substrates, NW- and NT-BBFs have been transferred to open frames with good orientational alignment of the NW and NT materials (Figure 5.16(g)), thus demonstrating the great flexibility of this approach.

Importantly, the BBF method is of great potential to be used for large-scale assembly of NWs. A representative image of an SWNT-BBF transferred to a 200-mm wafer (Figure 5.16(f)) shows that the film is remarkably uniform given the unsophisticated transfer process. Moreover, dark-field optical images (insets, Figure 5.16(f)) demonstrate that the SWCNTs have the same orientation and uniform separation across the diameter of this large substrate. Si NW-BBFs were also transferred uniformly, with good control of the Si NW alignment and density, to a large rectangular 225 × 300 mm plastic sheet substrate (Figure 5.16(h)). A histogram of angle distribution of over 400 Si NWs taken from different locations over the entire plastic substrate

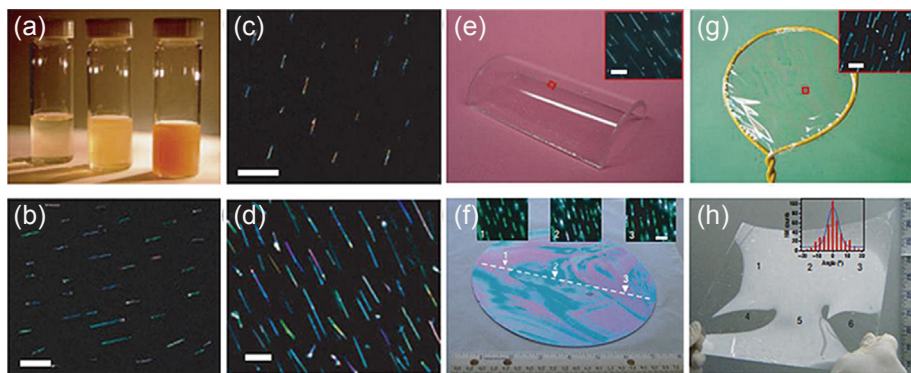


Figure 5.16 Density control of aligned NWs in BBFs and transfer of the NW arrays onto different substrates. (a) Photograph of 0.01 wt%, 0.03 wt%, and 0.15 wt% (left to right) epoxy suspensions of Si NWs. (b)–(d) Dark-field optical images recorded from 0.01 wt% (b), 0.03 wt% (c), and 0.15 wt% (d) Si NW-BBFs, respectively. The scale bars in (b), (c), and (d) are 50, 20, and 10 μm , respectively. (e) Si NW-BBF transferred to a curved surface. (f) SWNT-BBF transferred to a 200-mm Si wafer and its line-scanning alignment analysis. (g) Si NW-BBF transferred to an open frame with diameter ~ 6 cm. (h) Si NW-BBF transferred to a 225 × 300 mm plastic substrate.

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shows that more than 85% of the NWs are aligned within $\pm 68^\circ$ of the primary expansion/alignment direction.

The BBF approach for fabricating NW array thin films has several distinct advantages over other assembly methods developed previously. First, this approach can be used as a general method to organize a broad range of nanomaterials with high-degree orientational alignment and controlled density, including a variety of semiconductor NWs, multiwalled NTs (MWNTs), and single-walled (SWNTs), and in principle could be applied to organize many other nanostructures such as nanobelts and nanoparticles. Second, the nanomaterial-incorporated BBFs can be transferred to virtually any substrates or surfaces over large areas, including crystalline wafers, flexible plastics, and highly curved surfaces, to make large-scale functional nanodevice arrays. Third, this approach is highly scalable with potential to achieve meter-scale dimensions given the potential of blown film extrusion technique well established in the plastics industry. This represents one of the most critical advances in large-scale assembly of nanomaterials necessary for ultimately realizing applications and efficient processing of these nanomaterials in electronics and optoelectronics. For instance, the BBF method-fabricated composite films with NWs aligned and controlled-density are promising material platforms for high-performance field effect transistors, various sensors, and some other modern nanoelectronics. These large NW arrays fabricated from transferred Si NW-BBFs demonstrate that this approach yields devices with reproducible properties necessary for integrated electronics, biological/chemical sensors, and displays.

5.10 Conclusions and perspectives

This chapter illustrates recent advances in developing methodologies to rationally assemble NWs into designed architectures and further integrate these aligned NWs to construct functional nanodevices. Several unique assembly methods to organize NWs into ordered structures are introduced, including LB technique, optical trapping, contact printing method, electric field or magnetic field-driven assembly, microfluidic method, chemical- or bio-driven assembly, and BBF method. These methods show great potential in organization of NWs with directional alignments and hierarchical structures. It has been clearly demonstrated that NWs are unique and powerful building blocks for realizing the promise of the bottom-up paradigm of nanotechnology. The NW-based nanosystems will continue to make future revolutionary impacts in many research areas from the life sciences and health care to information technology and energy science.

However, several drawbacks still exist for methods presented in this chapter. First, most of the methods cannot be used on a large scale, which hinders their further application in industry-scale fabrication of aligned NW-based devices. Only the BBF method could achieve the assembly of NWs at potential meter-scale level. Second, most of the methods thus far developed can realize the alignment of NWs with directional precision but without positional precision. The NWs can be aligned along

certain directions and even under angular control. However, the patterned arrays of NWs that call for the positional control of NWs on substrates cannot be easily achieved. Third, it is still difficult using the assembly techniques to organize NWs to a sematic pattern with NW end-to-end registry, which is important in the fabrication of nanoelectronics. The sematic pattern of aligned NWs could facilitate the deposition of electrodes at each end of the NW and is critically favored in industrial device manufacturing.

To solve these problems, new delicate assembly methods or a combination of a few existing approaches should be further developed. For example, with the assistance of biomolecules, one could potentially realize the assembly of NWs with positional control. Furthermore, methods for assembly of NWs could be complemented with other top-down techniques such as lithography to achieve higher control of NWs. By applying the lithography technique, the substrate could be treated by different chemicals and the patterned substrate could facilitate the positional control of NWs during alignment.

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Quantum transport in semiconductor nanowires

6

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6.1 Introduction

This chapter is devoted to the study of quantum transport in semiconductor nanowires, whose properties are strongly influenced by quantum confinement, tunneling, correlation effects, and interference phenomena. Indeed, many physical phenomena occurring in semiconductor nanowires like electron–phonon coupling, impurity scattering, and electrostatic effects are drastically influenced by the reduction of dimension. Physical effects will be analyzed through the scope of nanoelectronics applications where nanowire transistors represent a central architecture to reach the end of the International Technology Roadmap for Semiconductor (ITRS).

Quantum effects and intrinsic fluctuations introduced by the discreteness of electronic charge and atoms will be major factors affecting the scaling and integration of such devices as they approach nanodimensions. For instance, variations in the number and position of dopant atoms in the active and source/drain regions make each nanowire transistor microscopically different from its neighbors (Asenov, 1998). The introduction of new materials such as SiGe or high- κ oxide induces additional sources of fluctuations associated with random variations in the structure, defects, strain, and inelastic scattering (Kuhn, Murthy, Kotlyar, & Kuhn, 2010). Apart from nano-nanoelectronics, semiconductor nanowires present other promising applications for solar cells (Tian, Kempa, & Lieber, 2009) or nanosensors (Xie, Xiong, Fang, Qing, & Lieber, 2012). These points will be discussed in other chapters of this book.

In that context, theory and simulation can contribute to the understanding of the physical phenomena occurring in the variety of nanowire architectures. Among the different theoretical approaches, the quantum nonequilibrium Green's function (NEGF) formalism is probably the most adapted to treat transport in nanostructures. The first section of this chapter will briefly describe this formalism, starting from the general Landauer approach.

Based on this formalism the following physical phenomena will be analyzed:

- Interface-induced correlation effects: In an inhomogeneous dielectric environment, the electronic structure of a particle in the semiconductor nanowire has to be corrected by image charge effects. Indeed, an added electron repulses nearby valence electrons and receives a “Coulomb hole” positive charge. In a bulk semiconductor, the valence electrons are “repulsed” to infinity and therefore do not interact with the added carrier. In an inhomogeneous dielectric environment, they are pushed to the surfaces of the system or to the dielectric interfaces, resulting in distribution of “image charges” at a finite distance from the carrier.

The interaction of the carrier with these own additional image charges generates corrections of the energy band structure. As we will see in [Section 6.3](#), this effect can have a strong impact on the transport properties of a nanowire.

- Ionized dopant atoms: changes in the number and position of the dopant atoms in the active region make each nanowire microscopically different from its neighbors, thus generating a high variability of its physical properties and in particular of its current characteristics. An initial study at the University of Glasgow ([Martinez et al., 2007](#)) showed in the case of silicon nanowire transistor that the trapping of a single electron in the active region could change the current by more than a decade. Since then, other studies evaluated the influence of randomly positioned dopants in the access source and drain regions of nanowire transistors ([Martinez, Seoane, Brown, Barker, & Asenov, 2009, 2010](#)). In this part, we will focus on the influence of a single ionized impurity located in the channel for both n- and p-type silicon nanowire transistors. Analysis of the current characteristics will show for instance an interesting phenomenon of negative differential resistance ([Bescond, Lannoo, Raymond, & Michelini, 2010](#)) and a current hysteresis effect ([Mil'nikov, Mori, Kamakura, & Ezaki, 2009](#)). [Section 6.4](#) presents these results.
- Electron–phonon (e–ph) coupling and self-heating effect: Electron–phonon interactions have an essential impact in semiconductor nanowires operating at room temperature. Their influence has been intensely analyzed in particular for nanotransistor applications where self-heating also plays an important role. Phonon-limited mobility has been calculated with the Boltzmann transport equation and has shown a strong reduction with respect to the bulk values for Si ([Neophytou & Kosina, 2011; Niquet, Delerue, Rideau, & Videau, 2012](#)). Within the NEGF formalism, e–ph coupling is usually described based on the self-consistent Born approximation (SCBA). We will discuss in [Section 6.5](#) the most suited crystallographic orientations to obtain the highest electron and hole mobilities before describing the issue of self-heating effect on current characteristics.

6.2 Theory and modeling

Nanowires are quasi-1D systems whose transverse dimensions easily reach the nanometer scale. Charge carriers be then in the mesoscopic transport regime where dimensions of the system are comparable to the characteristic lengths of the material, that is, the de Broglie wavelength and the mean free path. In the ultimate scaling configuration, carriers transit from one contact to another without any collision—this is the so-called ballistic transport regime. The Landauer approach was the first to provide a theoretical framework for this regime. In that approach the active region is described by a black box that electrons/holes can cross at a given energy with a given probability.

We will first demonstrate the Landauer formula before describing the equivalent approach implemented within the NEGF formalism. The formalism of nonequilibrium Green's functions (also called Keldysh or Kadanoff–Baym formalism), provides a suitable conceptual framework to treat electron–phonon, electron–photon, and even electron–electron interactions, which are likely to play an important role in realistic nanostructures.

6.2.1 The Landauer approach

Let us consider the case of a conductor connected to two large electronic reservoirs (Figure 6.1). The reservoirs are assumed to behave like a blackbody in optics—they perfectly thermalize any incident electrons by absorbing them without any reflection. The distribution of electrons arriving at a reservoir instantaneously reaches the equilibrium through “perfectly efficient” inelastic collisions. Moreover, transport is assumed to be ballistic in the active region, that is, it is coherent and elastic. At first, we also assume that there is no internal reflection; the conductor is “perfect” and the probability that an electron injected from one reservoir reaches the other is equal to 1. The current can be then calculated by considering a particular mode of the one-dimensional system $|i(k)\rangle$ propagating to the right, occupied according to the distribution function of the left reservoir $f(\varepsilon - \mu_L)$. Since a free-electron gas with n electrons per unit length moving at a speed v carries a current equal to $-nev$ and that the electron density of such a state $|i(k)\rangle$ is $1/L$ (for a conductor of length L), the current I^+ flowing from the left to the right is

$$I^+ = -\frac{e}{L} \sum_i v_i f(\varepsilon_i - \mu_L) = -\frac{e}{L} \sum_i \frac{1}{\hbar} \left(\frac{\partial \varepsilon}{\partial k} \right)_i f(\varepsilon_i - \mu_L). \quad (6.1)$$

We transform the sum over states $|i(k)\rangle$ by an integral in the mode-space:

$$\sum_k \rightarrow \frac{L}{2\pi} \int dk, \quad (6.2)$$

and obtain

$$I^+ = -\frac{e}{\hbar} \int_{-\infty}^{+\infty} f(\varepsilon - \mu_L) d\varepsilon. \quad (6.3)$$

If we consider a finite number N of modes, the partial current coming from the left reservoir is

$$I^+ = -\frac{e}{\hbar} \int_{-\infty}^{+\infty} N f(\varepsilon - \mu_L) d\varepsilon. \quad (6.4a)$$

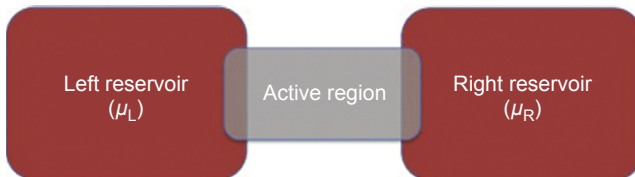


Figure 6.1 Nanoconductor (active region) connected to two semi-infinite reservoirs assumed at the thermal equilibrium with electrochemical potentials μ_L and μ_R for left and right, respectively. The applied bias V is defined as $-eV = \mu_L - \mu_R$ (e being the electronic charge).

A similar definition of the free states emitted by the right reservoir gives the partial current I^- :

$$I^- = +\frac{e}{\hbar} \int_{-\infty}^{+\infty} N f(\varepsilon - \mu_R) d\varepsilon. \quad (6.4b)$$

Finally, the total current is equal to the sum of the two components:

$$I = I^+ + I^- = -\frac{e}{\hbar} \int_{-\infty}^{+\infty} N(f(\varepsilon - \mu_L) - f(\varepsilon - \mu_R)) d\varepsilon. \quad (6.4c)$$

If the conductor is no longer “perfect,” the probability T that the electron injected from a reservoir is transmitted to the other is smaller than 1. A balance of the different current components leads to the following formula:

$$I = I^+ + I^- = -\frac{e}{\hbar} \int_{-\infty}^{+\infty} T N(f(\varepsilon - \mu_L) - f(\varepsilon - \mu_R)) d\varepsilon. \quad (6.5)$$

Equation (6.5) is the so-called Landauer formula that is widely used to describe transport in mesoscopic systems in which inelastic interactions are neglected (Büttiker, Imry, Landauer, & Pinhas, 1985).

6.2.2 The nonequilibrium Green's function formalism

Unfortunately, at the mesoscopic scale, particles are likely to undergo few inelastic interactions in the active region of the system. Moreover, interactions induce modifications of both location and energy of the charge carriers, making transport properties more difficult to analyze and thus to predict. The NEGF formalism quickly emerged as an effective quantum approach capable of modeling the scattering of charge carriers in nanoscale structures. This formalism was first introduced by Keldysh (1965) and Kadanoff–Baym (1962). The next section briefly introduces the central concepts of this method.

6.2.2.1 Definition of the different Green's functions

Let us first define the operators of creation $\hat{c}_k^+$ and destruction $\hat{c}_k$ acting on the fermion state $|k\rangle$ of the Hilbert space. Key relationships between these two operators are

demonstrated in various quantum mechanics books, including [Haug and Jauho \(1996, p. 35\)](#). The associated field operators are

$$\begin{aligned}\widehat{\psi}(r) &= \sum_k u_k(r) \widehat{c}_k, \\ \widehat{\psi}^+(r) &= \sum_k u_k^*(r) \widehat{c}_k^+, \end{aligned} \tag{6.6}$$

where r represents the spatial coordinate and u_k is a complete basis of the single particle eigenstates with the quantum index k .

In the Heisenberg representation, the field operator is written as a function of time t :

$$\widehat{\psi}(r, t) = e^{iHt/\hbar} \widehat{\psi}(r, t=0) e^{-iHt/\hbar}, \tag{6.7}$$

where H represents the Hamiltonian of the system. We can now define the time-dependent NEGF. There are four Green functions: “lesser” ($G^<$), “greater” ($G^>$), “retarded” (G^R), and “advanced” (G^A). Their expression with respect to the field operator is:

$$\begin{aligned} G^<(r_1, t_1, r_2, t_2) &= \frac{i}{\hbar} \langle \widehat{\psi}^+(r_2, t_2) \widehat{\psi}(r_1, t_1) \rangle, \\ G^>(r_1, t_1, r_2, t_2) &= -\frac{i}{\hbar} \langle \widehat{\psi}^+(r_1, t_1) \widehat{\psi}(r_2, t_2) \rangle, \\ G^R(r_1, t_1, r_2, t_2) &= -\frac{i}{\hbar} \Theta(t_1 - t_2) \langle \widehat{\psi}(r_2, t_2) \widehat{\psi}^+(r_1, t_1) - \widehat{\psi}^+(r_2, t_2) \widehat{\psi}(r_1, t_1) \rangle, \\ G^A(r_1, t_1, r_2, t_2) &= \frac{i}{\hbar} \Theta(t_2 - t_1) \langle \widehat{\psi}(r_1, t_1) \widehat{\psi}^+(r_2, t_2) - \widehat{\psi}^+(r_2, t_2) \widehat{\psi}(r_1, t_1) \rangle, \end{aligned} \tag{6.8}$$

where $\Theta(t_1 - t_2) = 1$ if $t_1 > t_2$, 0 otherwise.

In permanent regime, the previous Green’s functions only depend on the difference between t_1 and t_2 ($\tau = t_1 - t_2$) and it is then possible to use the Fourier transform:

$$G(r_1, r_2, E) = \int d\tau e^{iE\tau/\hbar} G(r_1, r_2, \tau). \tag{6.9}$$

We will adopt this notation in the rest of this section.

6.2.2.2 Kinetic equations

Within the NEGF formalism, transport of charge carriers is described by the so-called equations of Dyson:

$$[E - H(r_1) - eV(r_1)]G^R(r_1, r_2, E) - \int \partial r \Sigma^R(r_1, r, E)G^R(r, r_2, E) = \delta(r_1 - r_2), \quad (6.10)$$

and Keldysh:

$$G^{<, >}(r_1, r_2, E) = \int \partial r \int \partial r' G^R(r_1, r, E) \Sigma^{<, >}(r, r', E) G^{R+}(r', r_2, E), \quad (6.11)$$

where $H(r_1)$ represents the single particle Hamiltonian of the active region of the system (i.e., the region that is not at equilibrium), $V(r_1)$ is the electrostatic potential, E is the energy of the considered particle, and $\Sigma^{R, <, >}$ are the retarded, lesser, and greater self-energies of the particle, respectively. In the case of nanowires, self-energies define (1) the coupling of the semi-infinite reservoirs to the active region, and (2) the scattering (e.g., interactions between electrons/holes with phonons/photons). The general expression of the retarded self-energies (of both contacts and interactions) is the following:

$$\Sigma^R(r_1, r_2, E) = -\frac{i}{2}\Gamma(r_1, r_2, E) + P \int_{-\infty}^{+\infty} \frac{\partial E' \Gamma(r_1, r_2, E')}{E - E'}, \quad (6.12)$$

where P represents the Cauchy principal value integral. We then deduce the expression of Γ :

$$\Gamma(r_1, r_2, E) = i(\Sigma^R(r_1, r_2, E) - \Sigma^{R+}(r_1, r_2, E)). \quad (6.13)$$

From a physical point of view, Γ defines the broadening of the energy levels of the system due to the coupling with the reservoirs and/or to the inelastic interactions (with phonons/photons).

Equations (6.10) and (6.11) can be rewritten in a matrix form in any local basis (i.e., atomic orbitals, discretized operators in finite differences, etc.). If we distinguish the self-energies associated to the contacts (Σ_C) from those associated to the interactions (Σ_I), we obtain

$$[G^R(E)] = \left(E[I] - [H] - [V] - [\Sigma_C^R(E)] - [\Sigma_I^R(E)] \right)^{-1}, \quad (6.14)$$

$$[G^{<, >}(E)] = [G^R(E)] \left([\Sigma_C^{<, >}(E) + \Sigma_I^{<, >}(E)] \right) [G^R(E)]^+. \quad (6.15)$$

The calculation of the self-energies of the reservoirs can be exactly performed. For a more detailed description, see [Ferry, Goodnick, and Bird \(2009\)](#). On the other hand, self-energies of interactions are usually much more complicated to implement. For instance, interactions between electrons/holes and phonons are usually calculated within a numerically expensive SCBA. Within this approximation the self-energy $\Sigma_I^{<,>}(E)$ is linearly dependent of $G^{<,>}(E)$. [Equation \(6.15\)](#) then requires a self-consistent loop, called the Born approximation, to be solved. The reader will find additional details in [Ferry et al. \(2009\)](#) and [Haug and Jauho \(1996\)](#).

6.2.2.3 Carrier density and current calculations

Based on the previous equations, the main physical transport properties can be obtained. For instance, one can calculate the local density of states (LDOS) in each transverse slice (or atomic plane) of the active region:

$$\rho_P(E) = \text{Tr}[A_{P,P}(E)],$$

$$[A] = i \left([G^R] - [G^A]^\dagger \right), \quad (6.16)$$

where $[A]$ is the spectral function and Tr the trace over the orbitals or mesh points of the transverse plane P . Density of electrons (holes) at the mesh point i, j, k is then obtained as

$$n^{(p)}_{i,j,k} = -\frac{i}{\Omega} \int \frac{dE}{2\pi} \text{Tr} \left[G_{i,j,k}^{<(>)}(E) \right], \quad (6.17)$$

where Ω represents the volume of the discretized cell. The trace operates on the terms of the chosen local basis at the spatial point i, j, k . Finally, the current of electrons (holes) transmitted between two consecutive slices or atomic planes P and $P + 1$ is calculated as follows:

$$J_{P,P+1}^{n(p)} = \frac{e}{\hbar} \int \frac{dE}{2\pi} \text{Tr} \left\{ [\beta_{P,P+1}] [G_{P+1,P}^{<(>)}(E)] - [\beta_{P+1,P}] [G_{P,P+1}^{<(>)}(E)] \right\}, \quad (6.18)$$

where $[\beta_{P,P+1}]$ is the coupling matrix between the planes P and $P + 1$.

6.2.2.4 Electron–electron interactions

Electron–electron interactions have a strong influence in nanowires. They can be treated within a many-body approach, but the problem rapidly becomes too tricky to treat realistic systems. Most of the time they are described via a mean-field approach where the system is described by a single electron Schrödinger equation. Within this approach, the potential $V(r)$ depends on the carrier density. For instance, this is the case of the Hartree approximation that is equivalent to the self-consistent resolution of the Schrödinger–Poisson equations. Indeed, the connection of the nanostructure to two

reservoirs with different electrochemical potentials induces variations of both electronic density and electrostatic potential that have to be self-consistently calculated. In this approach, electron–electron (hole–hole) interactions are characterized by the dielectric constant ϵ of the semiconductor:

$$\nabla \cdot (\epsilon(r) \nabla V(r)) = -\rho(r), \quad (6.19)$$

where V is the electrostatic potential and ρ the 3D charge density. The Poisson equation is then self-consistently coupled to Eqn (6.17).

Based on this theoretical framework, we will investigate in the next sections some important physical effects occurring in semiconductor nanowires, starting with the interface-induced correlation effects.

6.3 Interface-induced correlation effects

The reduction of the size of nanowires and the introduction of new materials (such as oxides with high permittivity) generates strong dielectric inhomogeneities whose impact on transport properties is difficult to assess. Understanding the effects of the dielectric environment on the transport properties has in recent years attracted increasing attention (Diarra, Niquet, et al., 2007; Diarra, Delerue, et al., 2008; Niquet et al., 2006). These inhomogeneities may alter the transport properties and create a so-called “self-energy” correction whose amplitude is proportional to the ratio of the dielectric constants.

6.3.1 Physical origin

At the nanoscale, an electron added in the active region repels electrons in its vicinity toward the interfaces of the nanowire, leading to a so-called “image-charge” distribution. Interaction between the electron and its own image-charge distribution at the interface is a long-range correlation effect that is not described in conventional calculations for open systems in a nonequilibrium state (like the “Hartree” or “Hartree Fock” approximation). It must be normally described within a many-body approach such as the GW method of Hedin and Lundquist (Hedin, Lundquist, & Lundquist, 1971). Within this method, the single-particle Hamiltonian contains a nonlocal self-energy. This term considers the dynamic correlation effects and involves a screening that depends on the frequency of the electron–electron interactions via plasmon excitations (i.e., collective oscillations of an electron gas at a given frequency). Unfortunately, most of the calculations performed in nanoscale structures (including nanowires) are based on the self-consistent “Schrödinger–Poisson” approach (equivalent to the “Hartree” approximation). The correlation effects induced by the interfaces are nevertheless likely to play an important role in ultimate nanowires. GW calculations were first reported (Crampin, 2005; Rinke, Delaney, Garcia-Gonzalez, & Godby, 2004; Rohlfing, Wang, Krüger, & Pollmann, 2003) for the renormalization impurities levels near the

interfaces. Thereafter, the GW approach was naturally extended to nonequilibrium systems and expressed within the formalism of Keldysh Green's functions. This has been implemented for simple systems (Darancet, Ferretti, Mayou, & Olevano, 2007; Spataru, Hybertsen, Louie, & Millis, 2009), establishing a basis for a more accurate description of transport in nanostructures. However, a numerical implementation of this formalism for realistic devices and especially in nanowires is impossible due to computational limitations. Furthermore, it has been demonstrated (Delerue & Lannoo, 2004) that these effects were the result of long-range interface correlations that may be connected with good precision to the charging potential image.

6.3.2 The case of open systems

In open systems, the Hartree mean-field approximation does not include correlation effects corresponding to the repulsion of electrons in the vicinity of electrons moving in the active region. Electrons must then be considered as quasi-particles surrounded by a Coulomb hole. This phenomenon is equivalent to a dynamic screening where the instantaneous total electron density n_{tot} exhibits a decrease in the position of the electron r . When this electron rearrangement is sufficiently fast, it is possible to treat the screening of the charge as if it were static around the electron position. The features of this simple description, however, vary depending on the situation: (1) for a bulk metal, the charge screening is total and occurs over few Thomas–Fermi lengths. Conservation of the total charge implies that the charge compensating e (the electronic charge) is repelled to infinity; (2) for a bulk semiconductor, the screening is not complete. Beyond few Thomas–Fermi lengths from the electron, the potential behaves as $e/(e|r - r'|)$. The short-range screening corresponds to a Coulomb hole having a charge $-e(1 - 1/\epsilon)$, and a compensatory charge $e/(1 - 1/\epsilon)$ is repelled to infinity; (3) for a semiconductor with a finite size, the short-range screening still corresponds to a Coulomb charge $-e(1 - 1/\epsilon)$, but in this case the compensatory charge $e/(1 - 1/\epsilon)$ becomes an image-charge repelled to the boundaries of the material. The interaction of the additional carrier with its own image charges gives rise to a self-energy correction. This self-energy correction has been treated as a semiclassical screened self-energy in nanocrystals, thin films, and ideal nanowires and has shown an exact correction of the gap (Niquet et al., 2006; Delerue, Lannoo, & Allan, 2000) compared to ab initio calculations. This effect also has a strong influence on the ionization of the impurities in nanowires (Bjork, Schmid, Knoch, Riel, & Riess, 2008; Diarra, Niquet, et al., 2007). In the next subsection we will focus on the influence of this effect in realistic Si nanowire metal-oxide-semiconductor (MOS) transistors.

6.3.3 Influence in nanowire transistors

In order to illustrate the impact of interface-induced correlation effects in nanowires, we consider the Si nanowire transistor represented in Figure 6.2.

The self-energy correction is calculated and added to the usual electrostatic potential. The transport properties are then obtained from a self-consistent Poisson-NEGF approach described in the Section 6.2. Inelastic interactions are neglected.

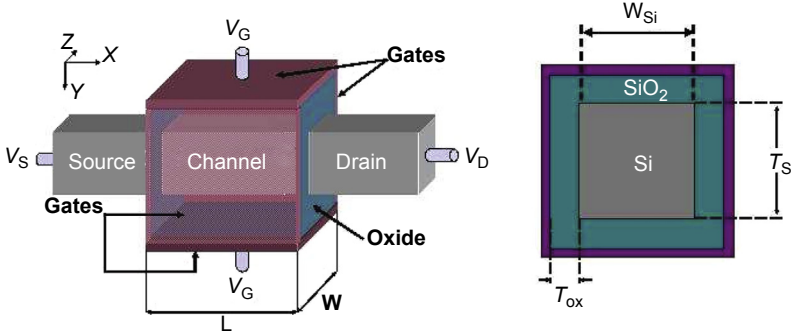


Figure 6.2 Structure of the n-type silicon nanowire MOSFET considered in this subsection. The wire is oriented along the $\langle 100 \rangle$ direction. The regions of source, channel, and drain are 8-nm long each. The oxide thickness is 1 nm. A continuous doping of $2 \times 10^{20} \text{ cm}^{-3}$ is assumed in the source and drain while the channel is intrinsic. Extracted with the permission of *Physical Review B*, 80, 195318 (2009). Copyright 2009 APS.

The self-energy correction Σ along the transport direction is shown in Figure 6.3 for different cross-sections. We first note that the calculated component is positive inside the silicon nanowire since $\epsilon_{\text{Si}} > \epsilon_{\text{ox}}^{\infty}$ (where $\epsilon_{\text{Si}} = 11.2 \times \epsilon_0$ is the dielectric constant of the silicon and $\epsilon_{\text{ox}}^{\infty} = 2.1 \times \epsilon_0$ is the dynamic dielectric constant that only contains the electronic contribution). The influence of the gate, which extends from 8 to 16 nm, is also clearly visible. It generates a stronger screening and then reduces the self-energy in the channel with respect to its value in the source and drain regions. For $T_{\text{Si}} = 4 \text{ nm}$, the influence of the interface is weak and Σ converges toward a constant and negligible

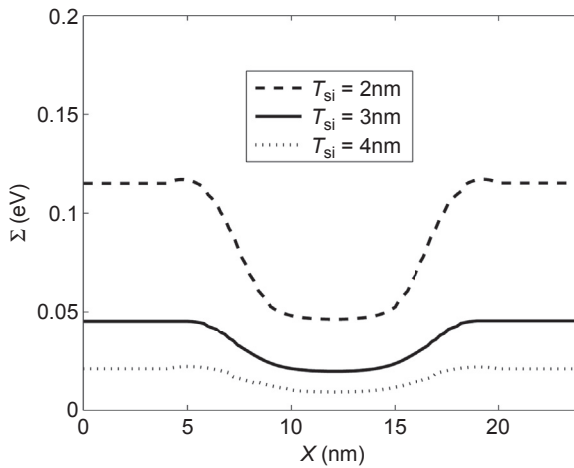


Figure 6.3 Interface-induced self-energy correction Σ along the transport direction for different cross-sections of silicon T_{Si} . The metal of the gate extends from 8 to 16 nm. Extracted with the permission of *Physical Review B*, 80, 195318 (2009). Copyright 2009 APS.

value along the source–drain axis. The electronic transport is not impacted. Reducing the silicon thickness from 4 to 2 nm promotes the dynamic screening of the gate in the channel, which accentuates the difference between the values of the self-energy in the channel and in the side regions (that reaches 0.07 eV at $T_{\text{Si}} = 2$ nm).

Figure 6.4 shows the first electronic sub-band with and without self-energy corrections for different gate voltages ($T_{\text{Si}} = 3$ nm). We observe a systematic reduction of the potential barrier in the channel whatever the applied gate voltage. To illustrate the dependence with the cross-section Figure 6.5 shows the modifications of the first sub-band with $T_{\text{Si}} = 4$ and 2 nm for two different gate voltages (in the off- and the on-regime). We note that Σ has a marginal influence in 4-nm wire while the channel barrier undergoes a significant decrease of nearly 0.1 eV in device of $T_{\text{Si}} = 2$ nm, independently of the applied gate voltage. This has a direct effect on the current characteristics represented in linear and logarithmic scales in Figure 6.6. While the impact is fairly weak for a cross-section of $4 \times 4 \text{ nm}^2$, the self-energy correction greatly increases the current in nanowire of $2 \times 2 \text{ nm}^2$. This effect then has a significant impact in nanowire MOSFETS and must be taken into account when many materials are stacked, as in the case of metallic gate of transistors.

Based on the previous findings, we focus in the next part on the dependence of the interface correction with respect to the nature of material gate oxide.

Considering a SiO_2 gate oxide, Figure 6.7 shows the impact of Σ on the subthreshold slope and the threshold voltage as a function of T_{Si} . First of all, the reduction of the

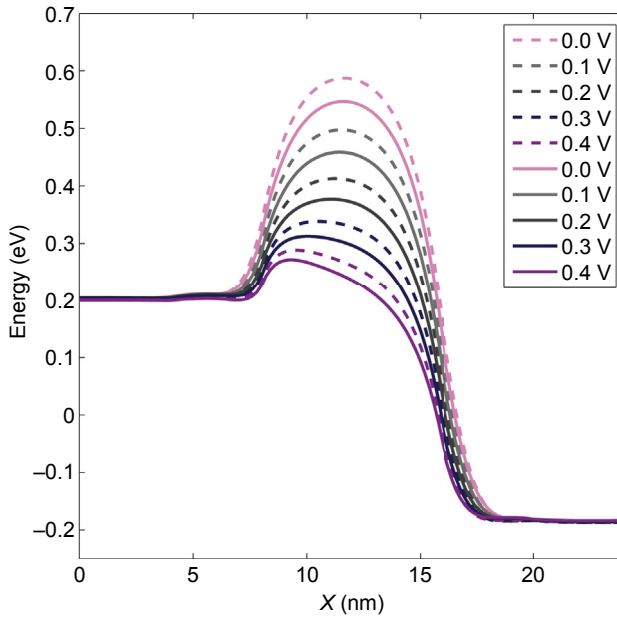


Figure 6.4 Profile of the first electronic sub-band for different applied gate voltages (from 0.0 V to 0.4 V) with Σ (solid line) and without Σ (dashed line). $T_{\text{Si}} = 3$ nm; $V_{\text{DS}} = 0.4$ V.

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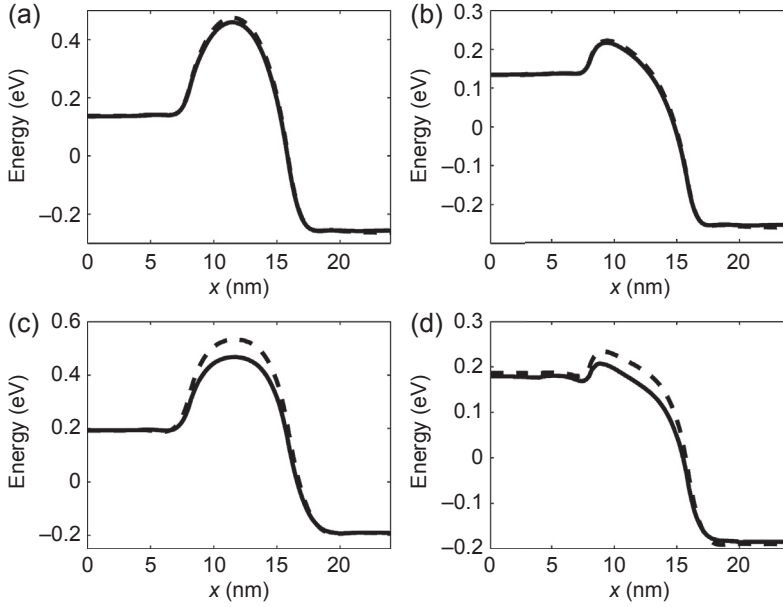


Figure 6.5 Profile of the first electronic sub-band with Σ (solid line) and without Σ (dashed line) for various parameters: (a) $T_{\text{Si}} = 4$ nm, $V_G = 0.0$ V; (b) $T_{\text{Si}} = 4$ nm, $V_G = 0.4$ V; (c) $T_{\text{Si}} = 2$ nm, $V_G = 0.0$ V; (d) $T_{\text{Si}} = 2$ nm, $V_G = 0.4$ V. $V_{\text{DS}} = 0.4$ V. Extracted with the permission of *Physical Review B*, 80, 195318 (2009). Copyright 2009 APS.

cross-section induces a decrease of the subthreshold slope regardless of the incorporation of the self-energy. Furthermore, the presence of correlation effects leads to an increase of the slope while the threshold voltage is strongly reduced. The difference of the threshold voltage ΔV_{TH} with and without the self-energy increases continuously with the decrease of the cross-section with a maximum value of 60 mV for $T_{\text{Si}} = 2$ nm.

Dependence of the electrical parameter can be significantly modified by the dielectric environment. We can for instance consider a nanowire transistor coated with a high- κ gate oxide (HfO_2 in the present case) instead of SiO_2 . We observed on [Figure 6.8](#) a similar dependence of the subthreshold slope and the threshold voltage than the one of a transistor incorporating a SiO_2 gate oxide. However, the amplitude of variations is much lower since HfO_2 acts more effectively as a dielectric protection with respect to the gate. The difference of the dielectric environment between the channel and the source/drain regions is less significant.

6.3.4 Conclusions

We discussed the importance of interface-induced correlation effects in realistic nanowire devices from a detailed investigation of the corresponding GW self-energy. In nanowires narrower than 4 nm, self-energy corrections significantly shift electronic sub-bands in the channel region, thus generating a large influence on the

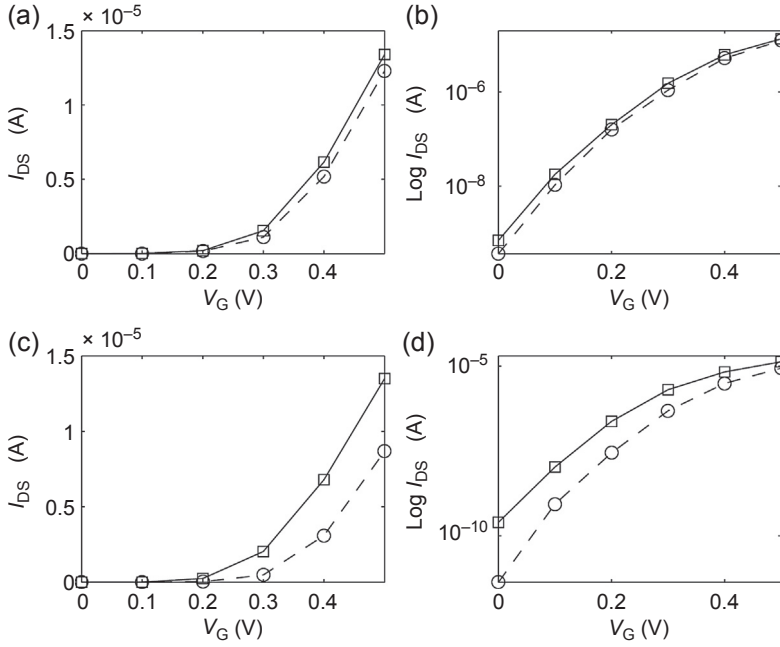


Figure 6.6 Comparison of $I_D(V_G)$ current characteristics with $V_{DS} = 0.4$ V for various nanowire transistors with (solid line) and without (dashed line) Σ . (a)–(b) $T_{Si} = 4$ nm; (c)–(d) $T_{Si} = 2$ nm.

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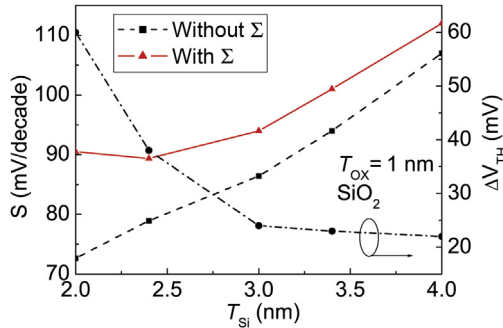


Figure 6.7 Subthreshold slope (S) and threshold voltage (ΔV_{TH}) as a function of the nanowire thickness (T_{Si}) for a nanowire embedded by SiO_2 ($T_{OX} = 1$ nm) with (solid line) and without (dashed line) Σ . $V_{DS} = 0.4$ V $\epsilon_{OX} = 3.9$, $\epsilon_{OX}^\infty = 2.1$, and $\epsilon_{Si} = 11.7$. ΔV_{TH} represents the difference between the threshold voltage with and without the self-energy corrections.

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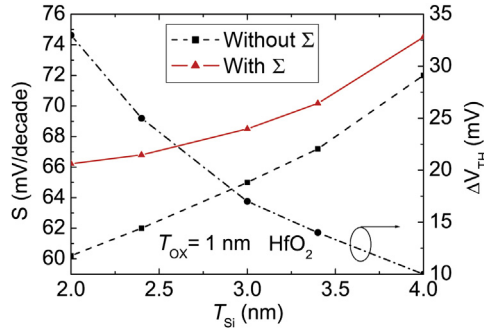


Figure 6.8 Subthreshold slope (S) and threshold voltage (ΔV_{TH}) as a function of the nanowire thickness (T_{Si}) for a nanowire embedded in HfO_2 ($T_{OX} = 1$ nm) with (solid line) and without (dashed line) Σ . $V_{DS} = 0.4$ V $\epsilon_{OX} = 26$, $\epsilon_{OX}^\infty = 5$, and $\epsilon_{Si} = 11.7$. ΔV_{TH} represents the difference between the threshold voltage with and without the self-energy corrections.

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current–voltage characteristics. From an electrical point of view, the presence of this effect reduces the subthreshold slope and the threshold voltage. However, the use of high- κ gate oxide materials can minimize the influence of the metallic gate and significantly reduces variations of these electrical parameters.

6.4 Transport through single ionized impurities

Dopant atom in nanowires is an important source of scattering that significantly modifies transport properties. Random fluctuations of the number of these dopants is already a major issue in the microelectronics industry (Khun et al., 2011). In this context, it is relevant to analyze the influence of a single impurity and try to take advantage of their presence in the active region to improve device performance or propose novel functionalities. In this part, we first analyze the transport through a single ionized impurity (of both donor- and acceptor-type) in n-type silicon nanowire MOS transistor. We illustrate the impact of the impurity position on the current characteristics and describe the involved phenomena. Then, we focus on p-type Si nanowire transistors and show that the ionized impurity amplifies the current variability due to strong interband coupling.

6.4.1 Transport of electrons: n-type nanowire transistors

We consider a single ionized impurity located in the channel of an n-type silicon nanowire transistor. The channel is oriented along the $\langle 100 \rangle$ direction, has a length of 9 nm, and a cross-section of 2×2 nm². Figure 6.9 shows the potential energy profile along the transport direction for three configurations of doping in the system.

Let us first focus on the influence of an acceptor impurity. This type of dopant is negatively charged and generates a positive Coulomb barrier that repels electrons

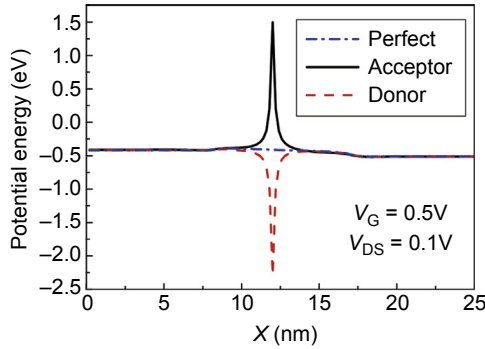


Figure 6.9 Potential energy profile along the transport axis in three cases: (1) the channel is intrinsic (dashed–dotted line), (2) with an acceptor impurity (solid line), (3) with a donor impurity (dashed line). The defect is in the middle of the channel and at the center of the cross-section. $V_G = 0.5$ V and $V_{DS} = 0.1$ V.

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from its vicinity. It thus reduces the current with respect to an intrinsic channel as shown in Figure 6.10.

Moreover, the amplitude of the current reduction strongly depends on the spatial position of the impurity. For example, the effect is larger when the acceptor is located at the center of the cross-section. Current characteristics are also strongly dependent on the position of the defect along the wire axis. In the case of transistors, the maximum decrease of the current is obtained when the impurity is located in the middle of the channel and may achieve two orders of magnitude in ultra-narrow nanowires. On the other hand, the influence of the dopant is almost negligible when it is located near the heavily doped source and drain regions.

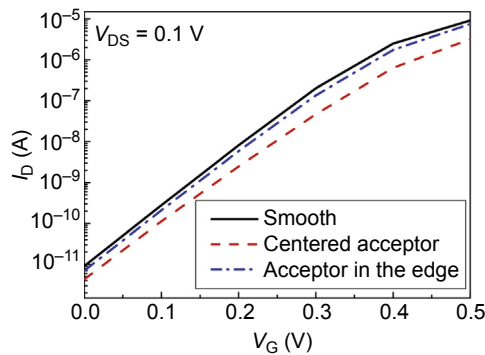


Figure 6.10 Current characteristics resulting from three doping configurations: without impurity in the channel (solid line), with an acceptor-type impurity in the center of the cross-section (dashed line), with an acceptor-type impurity located on the edges of the cross-section (dashed + dotted line). $V_{DS} = 0.1$ V.

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The case of the donor is substantially different since it creates an attractive Coulomb potential (Figure 6.9) that induces quasi-localized states in each electronic sub-band generated by the transverse potential confinement. These additional “donor states” are spatially localized near the defect but are not “real” bound states. They can in particular give rise to interactions with the energy continuum of the contacts as shown in Figure 6.11, which compares the transmission coefficients with and without dopant.

The intrinsic device (i.e., without point defect in the channel) is characterized by the usual step-like shape that corresponds to the quantization transverse states and gives rise to the quantum of conductance. The presence of a single donor generates a dip in each step of the transmission. Figure 6.12 explains this effect by showing the transmission coefficients for V_G ranging from 0.1 to 0.6 V. We first note that the quasi-resonances are shifted to lower energies when the voltage gate increases. Furthermore, the nature of the resonances varies with the applied voltage. The donor potential successively induces resonance peaks ($V_G < 0.4$ V) and antiresonant dips (for $V_G > 0.5$ V). These resonances result from interferences between the states of the direct transport (continuum) and those of the resonant site (quasi-bound states induced by the impurity). The two situations are schematically described in Figure 6.13, which illustrates the first two electronic sub-bands along the source–drain axis. In the off-regime the barrier potential of the channel sets the quasi-bonded state of a given sub-band above the energy of the same sub-band at the source contact (solid arrows in Figure 6.13). It results in a resonant tunneling between electrons injected from the source into a sub-band (or mode) and its own quasi-bound state. This is a single-mode phenomenon.

In the on-regime (high V_G), the barrier channel is sufficiently small to shift the donor states below the sub-band at the source contact, allowing interaction with the electrons of the lower sub-band. In contrast to the resonant case, it is a multimode phenomenon.

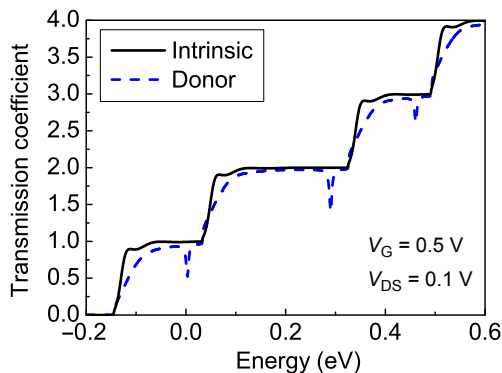


Figure 6.11 Transmission coefficient obtained for two configurations: without impurity (solid line), with a donor (dotted line). $V_G = 0.5$ V and $V_{DS} = 0.1$ V.

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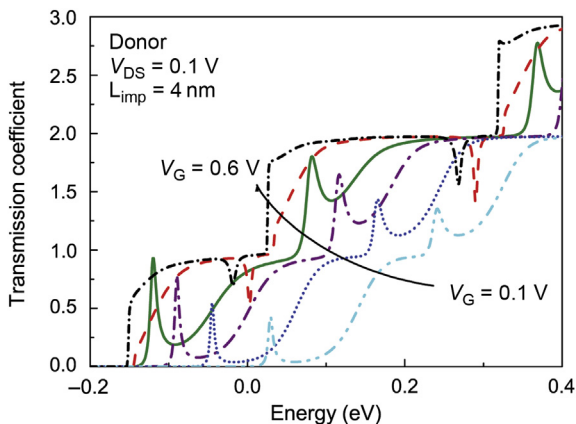


Figure 6.12 Transmission coefficients calculated for V_G ranging from 0.1 to 0.6 V with steps of 0.1 V. The shift of the quasi-localized state to lower energies when increasing the gate voltage is clearly visible as well as the transition from resonant to antiresonant states at $V_G = 0.4$ V and $V_{DS} = 0.1$ V.

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The above resonances and antiresonances directly affect the current characteristics (Figure 6.14). By comparison with intrinsic device, the resonant tunneling effect increases the current at low V_G while dips in transmissions induce current reduction in the on-regime. Consequently, the on–off ratio of the current declines and transistor performances are degraded.

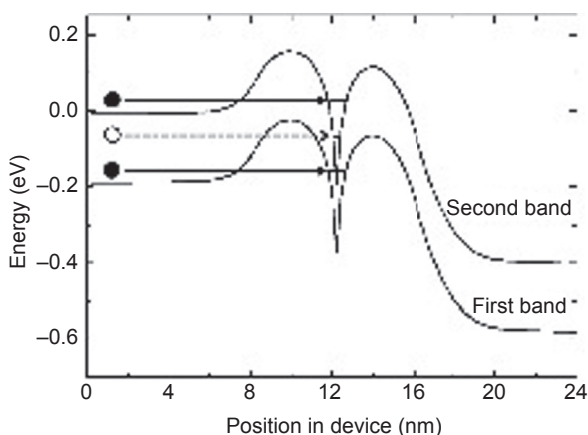


Figure 6.13 Schematic representation of the electron transport through an attracting Coulomb potential. Resonant transition (solid arrows) and antiresonant mechanism (dashed arrow).

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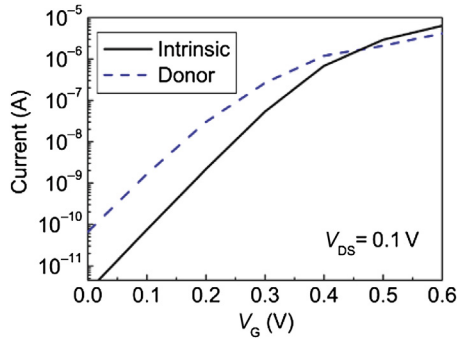


Figure 6.14 I_D – V_G characteristics without (solid line) and with (dashed line) the presence of a donor in the channel. The effects of resonance and antiresonance, respectively, generate an increase and decrease of current in the off- and on-regimes. $V_{DS} = 0.1$ V.

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It is, however, possible to take advantage of such quantum effects to obtain new functionalities of the device. For instance, the source–drain bias also represents a relevant parameter to modify the energies of the quasi-localized states. Figure 6.15 shows this dependence by plotting the transmission coefficient for two values of V_{DS} in the on-regime (high V_G).

We get another transition from resonant intramode processes at low V_{DS} to antiresonant multimode phenomena by increasing the bias. The impact on the current in this case is much more favorable since the I_D – V_{DS} curve exhibits a negative differential resistance (as shown in Figure 6.16).

Another interesting property of single donor nanowire transistor has been shown by Mil'nikov et al. (2009). They have theoretically predicted an intrinsic bistability resulting from two distinct screening mechanisms of the Coulomb potential impurity either

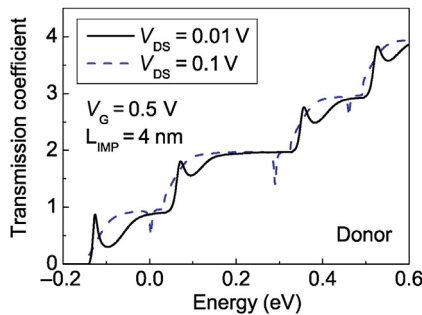


Figure 6.15 Transmission coefficients calculated for two drain voltages in the presence of a donor. Increasing V_{DS} reduces the energy quasi-bound states and generates antiresonances. $V_G = 0.4$ V.

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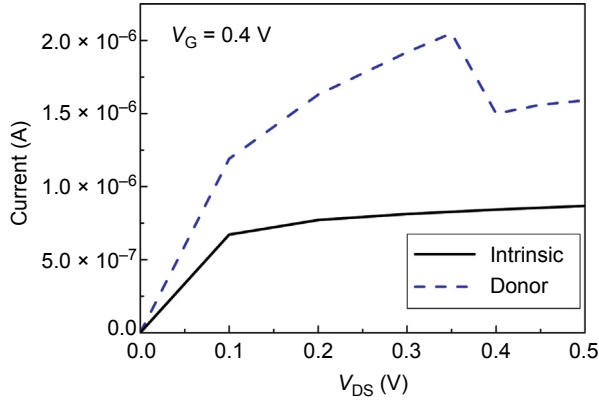


Figure 6.16 I_D – V_{DS} characteristics with (dashed line) and without (solid line) the presence of a donor in the default channel. The decrease of the current at $V_{DS} = 0.4$ V is due to the transition from a resonant to an antiresonant behavior when the Fermi level of the source is aligned with the defect level.

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by the source or by the drain electrons. Taken together, these results promote the idea that doped nanowire devices represent a great opportunity for various applications such as oscillators, amplifiers, or other bistable operations present in electronic circuits.

6.4.2 Transport of holes: p-type nanowire transistors

Hole transport is also essential in many applications like nanoelectronics or photovoltaics. However, accurate modeling of hole transport is more complicated than the one of their electron counterpart. Indeed, coupling of the first three valence bands in the bulk material (defined as “heavy hole,” “light hole,” and “spin–orbit”) introduces a strong nonparabolicity and anisotropy in the band structure. The situation is even more complicated when quantum confinement is present like in nanowires. Therefore, a more rigorous description of hole transport requires a so-called multiband Hamiltonian (including spin–orbit coupling). Figure 6.17 shows the calculated valence band with a six-band k.p Hamiltonian (Luttinger & Kohn, 1955).

Self-consistent Poisson-NEGF solver can be then implemented with this kind of Hamiltonian (Pons et al., 2011; Shin, 2009; Shin, Lee, & Klimeck, 2010). Figure 6.18 shows the resulting transmission coefficients for different gate voltages in an intrinsic channel p-type transistor. In the off-regime (from $V_G = 0$ V to $V_G = -0.3$ V), the transmission has a typical step-like shape (similar to the case of the electron conduction band) due to the discretization of conduction modes in quasi-1D systems. Surprisingly, transmission also presents peaks (e.g., at 0.3 eV for $V_G = 0$ V) that correspond to crossings and anticrossings of the valence band structure. This intersub-band

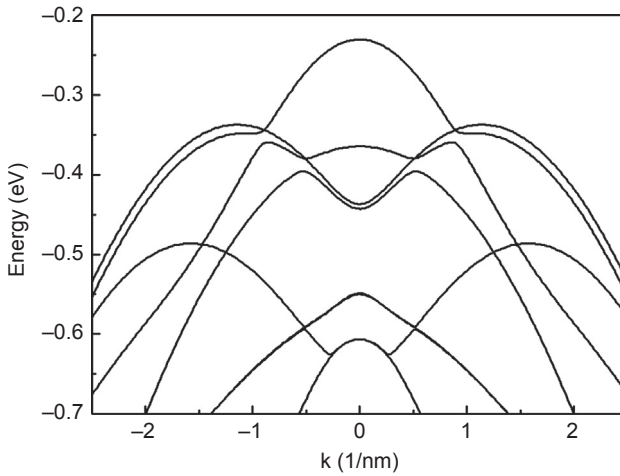


Figure 6.17 Six-band k.p band structure of the valence band for a Si nanowire oriented along the $\langle 100 \rangle$ direction with a $2 \times 2 \text{ nm}^2$ cross-section.

process has a stronger impact on the on-regime ($-V_G = 0.4 \text{ V} \rightarrow 0.6 \text{ V}$) for which the transmissions are substantially “peaked.” Indeed, the vicinity of the energy of the quasi-localized states in the channel with the corresponding bands in the source promotes intersub-band coupling. This intersub-band coupling thus represents an additional effect compared to n-type devices.

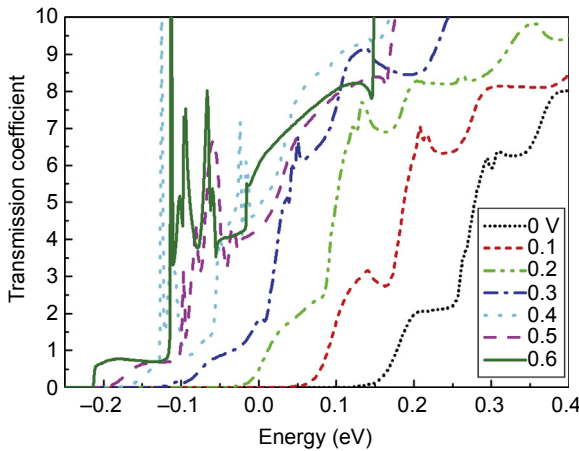


Figure 6.18 Transmission coefficients calculated for $-V_G$ ranging from 0 to 0.6 V with 0.1 V steps for an intrinsic channel p-type Si nanowire transistor. The transmission shift to lower energies when increasing the gate voltage is clearly visible as well as the transition to increasingly “peaked” transmissions. $V_{DS} = -0.4 \text{ V}$.

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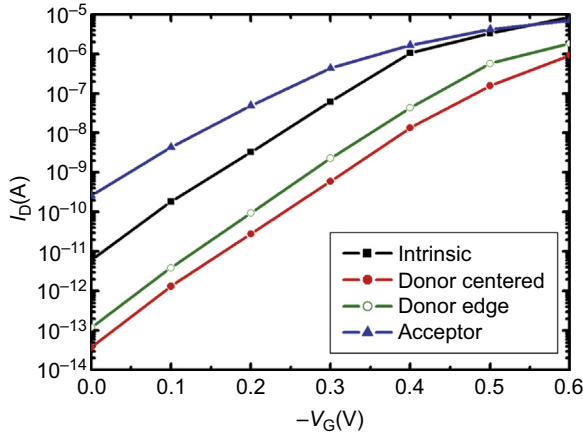


Figure 6.19 I_D – V_G characteristics of p-type nanowire MOSFETs without impurity (squares), with a donor (circles) and an acceptor in the middle of the transverse section of the channel (triangles) or on the edge of the cross-section (open circles). $V_{DS} = -0.4$ V. Extracted with the permission of *Applied Physics Letters*, 99, 082113 (2011). Copyright 2011 AIP.

We now add an ionized impurity in the channel of the same system. Figure 6.19 shows current characteristics for four different configurations: an intrinsic channel, with a donor or an acceptor in the center or on the edge of the cross-section. The presence of an ionized donor reduces the drain current of about two orders of magnitude. Symmetrically to the case of the acceptor in n-type devices, an ionized donor in a p-type nanowire generates a long-range repulsive potential for holes in the neighborhood, which strongly reduces the transmission. A donor then implies a reduction of current whose amplitude depends on its position. The same dependence is obtained as in the case of n-type devices. However intersub-band coupling in p-type devices increases the influence of the impurity on current characteristics and generates a larger reduction of the current.

An acceptor generates an attractive Coulomb potential that results in quasi-localized states through which quantum interferences occur (similarly to the case of a donor in an n-type transistor).

The LDOS, potential energy, and transmission are shown in the off-regime in Figure 6.20. We see that the peaks and dips of the transmission mainly correspond to the energies of acceptor quasi-localized states. Like in the case of n-type devices, the peaks are the result of a resonant tunneling between holes injected from the source in a sub-band and its own localized state. The antiresonant dips are induced by the interaction between the holes of a given sub-band and the localized state of a different sub-band. These phenomena still lead to higher off-currents than the intrinsic device (Figure 6.19). However, the conjugation of (1) interferences due to impurity and (2) intersub-band coupling already occurring in intrinsic channels generates strongly peaked transmissions. Therefore, Coulomb scattering is likely to introduce more variability in the p-type devices than in their n-type counterparts.

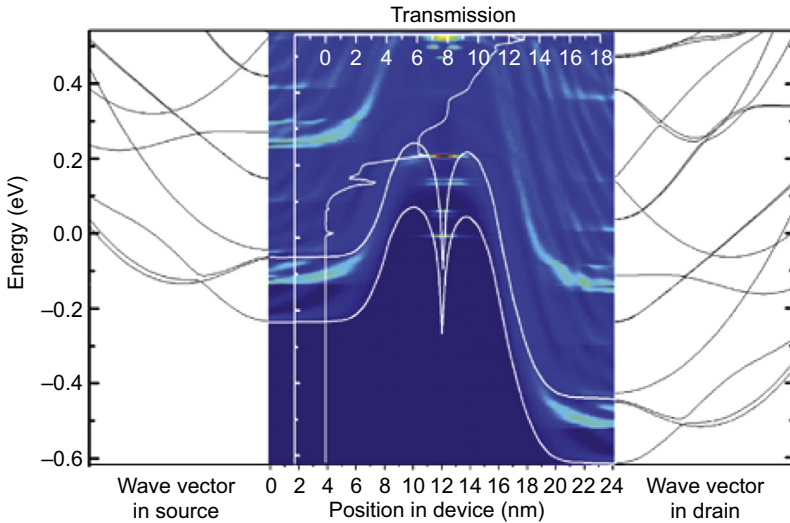


Figure 6.20 Local density of states, potential energy, and transmission coefficient of a p-type transistor with an acceptor in the middle of the transverse section. The sub-bands in the reservoirs are also represented. $V_{DS} = -0.4$ V and $V_G = 0$ V. For the sake of clarity, the band structures and the potentials are represented in terms of energy holes. Extracted with the permission of *Applied Physics Letters*, 99, 082113 (2011). Copyright 2011 AIP.

6.4.3 Conclusions

This section showed the influence of a single ionized impurity on the properties of n- and p-type nanowire transistors. For n-type nanowire MOS transistors, the position of an acceptor defect had a substantial impact on current reduction (up to two orders of magnitude). In the case of a donor-type impurity, a transition from resonant to antiresonant phenomena is obtained as a function of the applied voltages. This effect leads to a significant electrical performance degradation of the transistor. However, it can also be used to propose original functionalities like negative differential resistance or current hysteresis. Finally, intersub-band coupling is found to have an important impact in p-type nanowire transistors that might undergo a larger variability than their n-type counterparts.

6.5 Impact of phonon scattering

In the previous sections we analyzed the effects associated with interface-induced correlations and ionized impurities, which could significantly alter electrical characteristics of semiconductor nanowires. Regardless of these phenomena, interactions of electrons (or holes) with the lattice vibrations also have a strong importance at room temperature. This section first studies the influence of these interactions in nanowire transistors using the so-called “self-consistent born approximation” (SCBA) of the NEGF formalism. A second part will focus on the corresponding self-heating effect.

6.5.1 Phonon scattering at the nanometer scale

At the nanoscale, dimensions of the system reach the screening and scattering characteristics lengths of the material. The electrical resistance therefore deviates from the well-known Ohm's law that remains true in longer devices. At this scale, influence of interactions with phonons is no longer intuitive because of the dual dependence of the carriers in space and energy. Particles undergo few interactions in the active region making the effect on transport properties more difficult to analyze and thus to predict.

The NEGF formalism quickly emerged as an efficient quantum approach capable to model scattering of carriers by phonons in nanoscale structures. The so-called Keldysh formalism presented in [Section 6.2.2](#) is then used to describe the influence of phonon scattering in nanostructures and especially in nanowire transistors.

6.5.2 Influence of phonon scattering in silicon nanowire transistors

One of the first theoretical NEGF study focusing on phonon scattering in nanowire transistor was reported by [Jin, Park, and Min \(2006\)](#). The authors modeled n-type nanowire MOSFETs within the effective mass approximation. Their work showed that phonon scattering was most important in the on-regime. For a 15-nm gate length and a 5-nm cross-section transistor, the drain on current with phonon is found to be about 63% of its ballistic limit. On the other hand, the subthreshold region provides very similar currents. The effects of phonon scattering can be better understood by looking on the LDOS in the active region ([Figure 6.21](#)). In the ballistic limit, we see clear oscillations due to interferences of incident and reflected particles of the reservoirs. The transport is coherent. These oscillations are smoothed out when incorporating phonon scattering. The transport becomes dissipative. This behavior is also visible on the energy spectrum of the electron density ([Figure 6.22](#)). Phonon scattering then generates two main phenomena: carrier backscattering and carrier kinetic energy relaxation. Backscattering results from interactions with both acoustic and optical phonons, and it can take place along the whole active region. It is less likely to occur when electronic states on the source side are already occupied due to reflections, which explains that phonon scattering is less impacting in the subthreshold regime. On the other hand, carrier kinetic energy relaxation results from optical emissions and mainly occurs in the drain side ([Figure 6.21\(b\)](#)). Phonon scattering also induces a large broadening of the energy levels, which results in a nonzero electron density below the sub-band in the source and drain regions. We can also note that the current component can even increase through phonon-assisted phenomena permitting carriers to reach the thermionic regime ([Mori, Takeda, & Minari, 2008](#)).

The first fully atomistic simulations including electron–phonon scattering were reported by [Luisier and Klimeck \(2009\)](#). The authors developed a NEGF quantum transport solver based on $sp^3d^5s^*$ tight-binding model for holes and electrons and a Keating model for phonons. Considering a 15-nm gate length they studied in particular the degradation of the current with diameter ([Figure 6.23](#)).

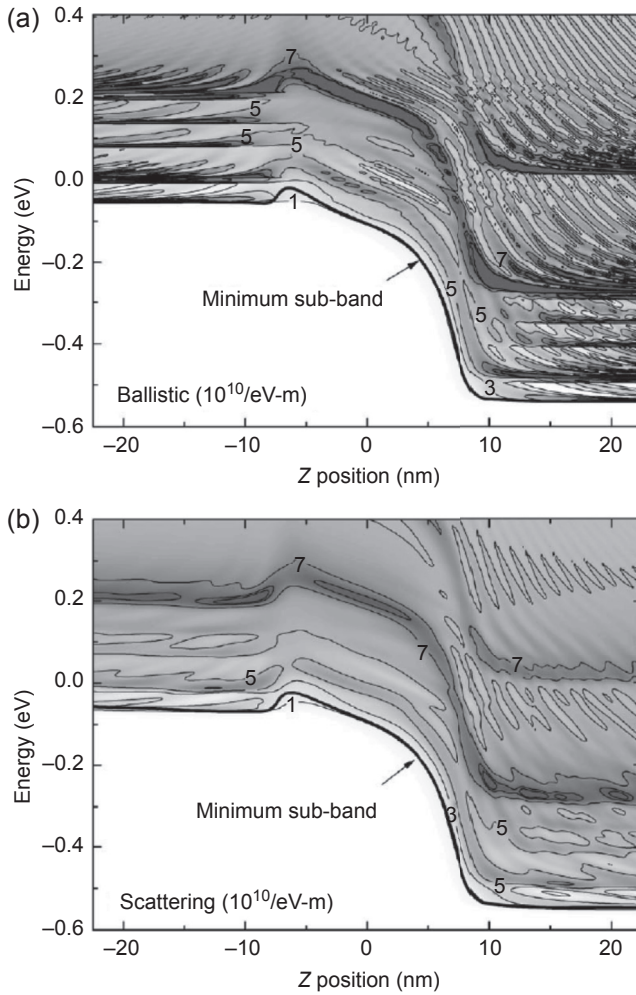


Figure 6.21 Local density of states of the n-type silicon nanowire transistor along the source-drain transport axis (a) in the ballistic limit and (b) in the presence of phonon scattering in the on-regime ($V_G = 0.3$ V and $V_{DS} = 0.5$ V).

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The study confirmed that phonon interactions are more significant in the on-regime and showed that phonon interactions are stronger in narrow nanowires. The same author ([Luisier, 2011](#)) investigated the most suitable nanowire orientation to optimize the phonon-limited mobility in ultrascaled n- and p-type Si nanowire transistors. According to their calculations, the [110] channel orientation represents the best compromise to improve both n-type and p-type nanowire transistor performances.

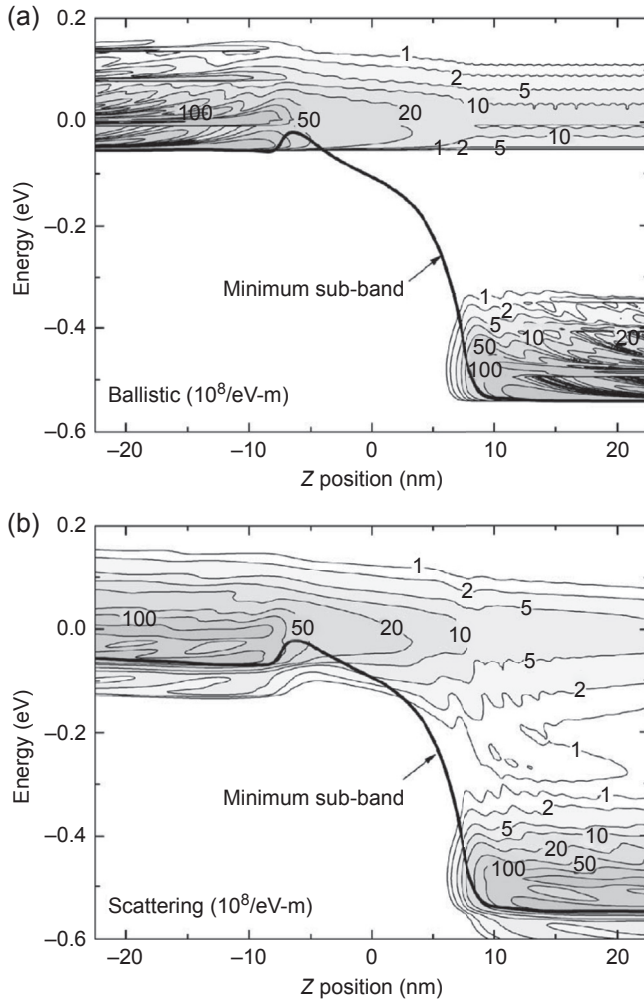


Figure 6.22 Energy spectrum of the one-dimensional electron density in nanowire transistor along the source–drain transport direction (a) in the ballistic limit and (b) in the presence of phonon interactions. $V_G = 0.3$ V and $V_{DS} = 0.5$ V.

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6.5.3 Self-heating

Another consequence of size reduction of nanowires is a tremendous growth of the heat generation ([Pop, 2010](#)). Indeed, high electric fields in devices generate hot carriers that transfer their energy to the lattice, leading to hot spots. These effects are strongly enhanced in nanoscale devices that sustain high current densities and include interfaces with materials of low thermal conductivity like SiO_2 ([Sadi, Kelsall, Pilgrim, Thobel, & Dessenne, 2012](#)). Structures based on semiconductor nanowires

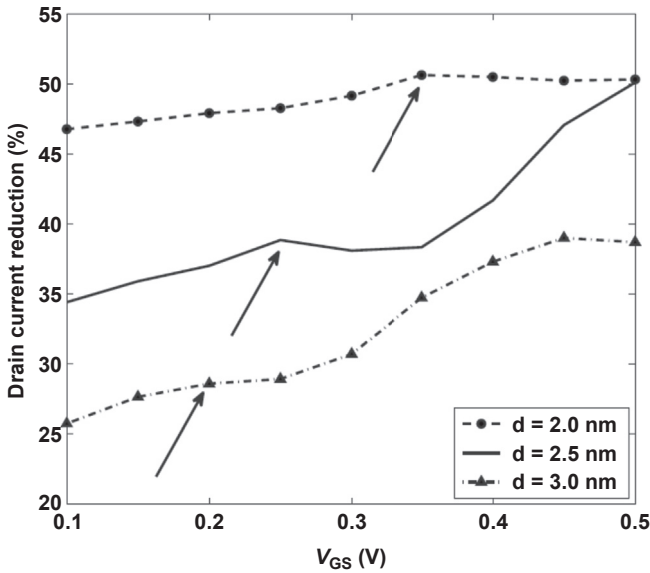


Figure 6.23 Drain current reduction due to phonon scattering for different diameters of n-type silicon nanowires. The reduction is calculated with respect to the ballistic value. $V_{DS} = 0.6$ V. Extracted with the permission of Luisier & Klimeck (2009). Copyright 2009 APS.

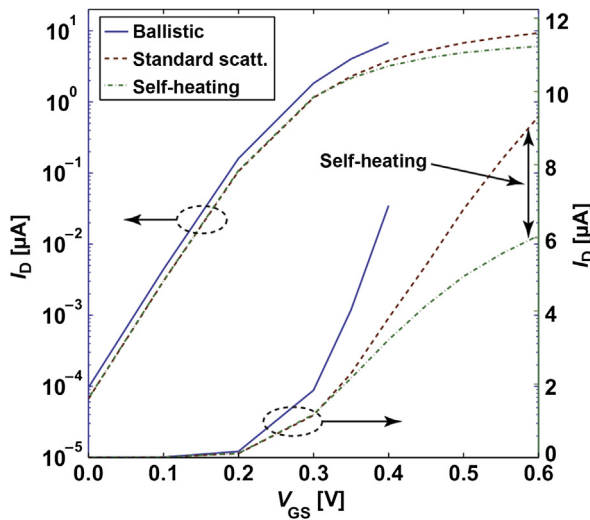


Figure 6.24 I_D – V_{GS} current characteristic of a Si nanowire transistor with a gate length of 15 nm and a diameter of 3 nm. Three current regimes are plotted: the ballistic one (solid line), the standard SCBA scattering (dashed line), and the self-heating one (dashed-dotted line). $V_{DS} = 0.6$ V.

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are one of the first affected by this effect. [Rhyner and Luisier \(2014\)](#) have recently coupled electron and phonon transport equations within the NEGF formalism. They found that driving phonons out of equilibrium induces substantial local variations of the temperature in the active region and an increase of the electron–phonon scattering strength. [Figure 6.24](#) shows the self-heating effects on the current characteristics of an n-type Si nanowire transistor. We see that the incorporation of the phonon scattering via the “usual” SCBA approach already reduces the on current by about 45% with respect to the ballistic limit. Driving the phonons out of equilibrium further reduces the current by another 30% (indicated by a double arrow on [Figure 6.24](#)).

Another relevant physical property that can be extracted from NEGF calculations is the electrical power dissipated and the maximum effective lattice temperature in the nanowire ([Figure 6.25](#)).

Both quantities increase with V_{GS} . The increase is more rapid for V_{GS} larger than 0.3 V, which correspond to the value of the threshold voltage of the transistor, where the self-heating starts to have a strong impact on the current (see [Figure 6.24](#)). The temperature also rapidly increases up to 500 K for V_{GS} , confirming that thermal balance will be a critical issue in strongly integrated nanowire devices.

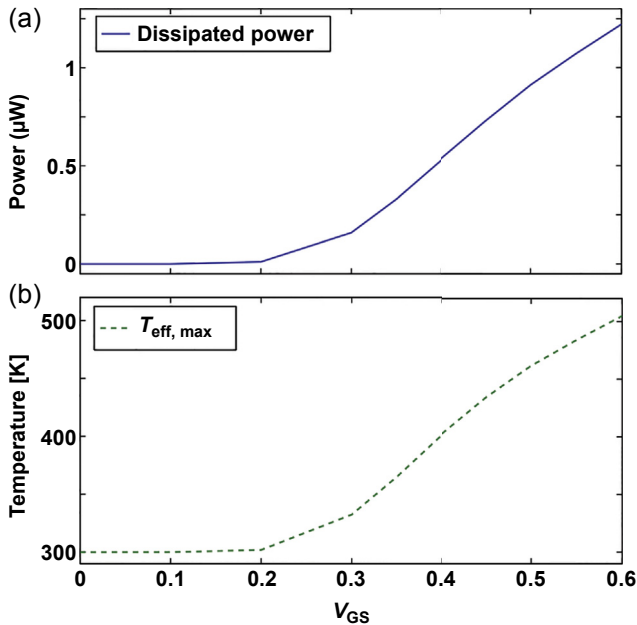


Figure 6.25 Evolution of the dissipated power (a) and the maximum effective temperature (b) as a function of V_{GS} for the Si nanowire transistor described in [Figure 6.24](#).

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Measuring the properties of semiconductor nanowires with transmission electron microscopy

7

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7.1 Sample preparation

Traditionally, preparation of samples with a suitable size and geometry has been one of the primary steps in transmission electron microscopy (TEM) characterization. However, nanowire geometry, especially applied as freestanding nanowires on a substrate, is ideally suited to TEM sample preparation and requires minimal processing. Nanowires naturally have dimensions suitable for transmission (one dimension thin compared with the electron mean free path while another dimension is sufficiently extended to allow the sample to be suspended over open holes in a grid). Nanowires can be easily transferred from substrates to TEM grids simply by touching the surfaces together, such that the extended nanostructures break from the substrate and land on the grid.

However, although it is simple and fast to break nanowires off from a substrate, it is often desirable to characterize the nanowire–substrate interface. To do so requires considerably more advanced preparation. Samples can be prepared by a conventional cleaving and iron milling procedure (Mårtensson, 2004). For more precise selection of nanowires, however, focus ion beam (FIB) milling can be used to produce well-defined TEM samples (Boulanger & LaPierre, 2012; Lenrick et al., 2014; Tomioka, Motohisa, Hara, & Fukui, 2008). This procedure requires considerable time and the yield of nanowires is naturally low.

Nanowire geometry can also lead to a radial symmetry of certain properties, such as composition, which are not ideally suited to characterization by transmission. This is especially important in the radial (core–shell) heterostructure class of semiconductor nanowires. In these materials, nanowire material is intentionally varied in a radial direction, resulting in compositional properties that vary in the viewing direction regardless of the nanowire orientation. To characterize this properly, it is necessary to view the nanowires along their axis rather than normal to it. Because the axis is much longer than the electron mean free path, this requires more careful sample preparation. The simplest way to produce cross-sectional samples is (ultra)microtomy, in which samples are embedded in a polymer resin and then sliced, typically with a diamond knife (Fakhr, 2012; Mohseni, Rodrigues, Galzerani, Pusep, & LaPierre, 2009; Sköld et al., 2006). Alternatively, FIB can also be used to produce well-defined slices from nanowires (Conesa-Boj et al., 2014; Verheijen, Immink, de Smet, Borgström, & BakkersVerheijen, 2006).

7.2 Structural properties

Development of semiconductor nanowire materials always requires routine characterization of the structure. This is especially true for binary nanowire materials (III–V and II–IV) that have a tendency to polytypism – that is, different crystal polytypes are common in nanowires and mixtures of different structures are common. Crystal structure can normally be determined simply by tilting the nanowire into a low-index zone and viewing the selective area diffraction (SAED) pattern. However, normally SAED is not local enough to fully identify local structural variations. Fortunately, the possible structural variations in semiconductor materials are well-known, and full analysis can typically be performed by analyzing the high-resolution TEM image in the low-index zone axis, along with its associated Fourier transform.

Most semiconductor nanowire materials grow preferentially in the close-packed direction (111-type in cubic structures and 0001 in hexagonal structures). In this direction, structure mixing often occurs in the growth direction, which makes it easy to characterize by viewing nanowires normal to their axis, and ideal for TEM. The cubic and hexagonal polytypes of binary semiconductors (zinc blende and wurtzite, respectively) can be easily distinguished by the stacking sequence of their bilayers in the [110] directions normal to their axis (Figure 7.1(a) and (b)). Because it is not necessary to distinguish the atomic layers making up each bilayer, the resolution required is

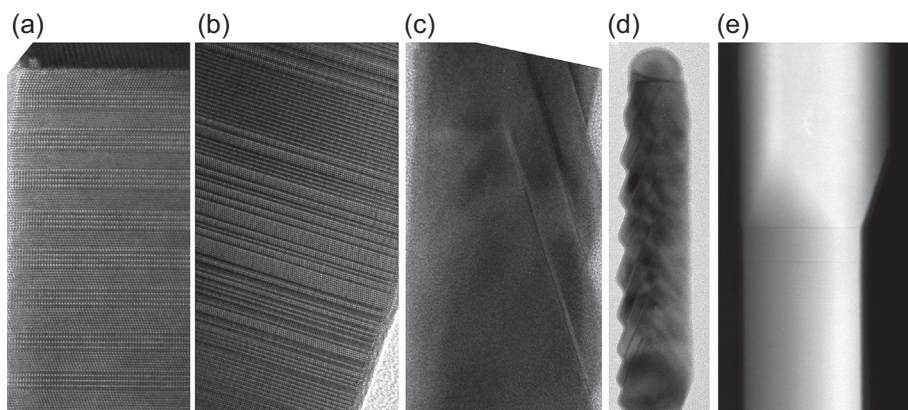


Figure 7.1 Structural and morphological analysis using standard techniques. (a,b) Crystal structure variations along the nanowire axis can be determined using conventional high-resolution TEM in an appropriate viewing direction, as shown here for InAs nanowires with controlled (a) and random (b) structural changes. (c,d) More thorough analysis is required for nanowires with structural changes, such as stacking defects, which are not normal to the nanowire axis (shown here for a GaSb nanowire). In this case, high-resolution and diffraction analysis must be performed from multiple viewing directions. (e) Morphology can often be identified by simple imaging using thickness contrast in high-angular annual darkfield scanning TEM (HAADF-STEM) if it does not vary on a local level. By tilting the nanowire into as few as two different viewing directions, the shape can often be determined. The nanowire in (e) is an InAs–InSb heterostructure.

moderate and most conventional high-resolution TEMs have sufficient resolution for routine analysis. The only requirement is that the sample be able to tilt to a sufficient degree so that typical nanowires can be aligned in a $\langle 110 \rangle$ direction.

7.2.1 *Advanced structural analysis*

High-resolution imaging in TEM uses the principle that electron waves interacting with a sample will exhibit a phase shift when they encounter a column of atoms. This phase-contrast gives the familiar atomic resolution image that appears in so many semiconductor nanowire publications. However, this type of image depends on the alignment of atoms into columns in the beam direction, with the column of atoms appearing as a single point in the resulting image. Any changes in the structure that interrupt the regular spacing of atoms along this column will necessarily complicate analysis of the resulting image. Because many semiconductor nanowire materials exhibit structural changes only along their axis, imaging normal to this direction avoids the complication of variations along an atomic column.

More advanced analysis is required if the nanowire materials exhibit structural variations such as stacking defects in other than the growth direction ([Figure 7.1\(d\) and \(e\)](#)). This is common for nanowires growing in directions other than the close-packed direction, and is also more common in group IV semiconductor nanowires. Careful analysis is thus required to determine the nature of the structure and stacking defects. Typically, nanowires must be imaged in more than one direction to fully interpret the structure correctly. For example, Si nanowires grown in a less-common direction such as $[112]$ or $[110]$ often exhibit lateral or inclined twin planes, and the prevalence of these or other types of twins is often associated with the type of metal catalyst particle used ([Conesa-Boj et al., 2010](#)). In some cases, twins may appear in intersecting directions and the resulting contrast may be difficult to interpret. For example, there has been considerable controversy regarding how to distinguish the appearance of overlapping twin domains from unusual polytypes in Si nanowires ([Cayron et al., 2009](#); [Lopez, Hemesath, & Lauhon, 2009](#)). To determine the structure correctly and unambiguously, detailed and extensive analysis is necessary.

For III–V semiconductor materials, growth in alternative (to the close-packed) directions is rare and rotational twinning is by far the dominant defect type. However, in some cases even this type of structure requires more detailed analysis for correct characterization. For example, III–V nanowires grown on a nonpolar substrate such as Si will have a variety of equivalent close-packed direction from which to choose and may spontaneously change between these in the initial stages of growth. This can occur via multiple-order twinning, which then must be carefully analyzed to fully understand the growth process ([Uccelli et al., 2011](#)).

7.2.2 *Polarity determination*

For most routine structural analyses, it is not necessary to separate the atomic layers making up a bilayer. However, for binary semiconductors such as III–V, the two atoms making up a bilayer are different (one III and one V atom per pair), and layers

therefore have a specific polarity. Determination of polarity in binary semiconductor nanowires has important implications for final nanowire properties and for understanding the growth process (Fernandez-Garido et al., 2012). However, the spacing of atoms in a bilayer is small, and more advanced techniques are necessary to distinguish them.

One relatively simple method of determining polarity is by convergent beam electron diffraction (CBED). This method uses an electron beam converged to a small probe, such that the resulting diffraction pattern contains discs associated with each crystallographic reflection. Because the probe contains electrons entering the sample at many slightly different angles, the discs have a fine structure originating from minor differences in the interaction of electrons with atoms in the sample from different angles. In polar materials, the density of the different atom types on planes may be different in different directions, resulting in characteristic patterns within the discs that depend on the polarity. The CBED patterns obtained from a nanowire sample oriented in a known direction can then be compared with simulated patterns to identify the polarity. This method has been used to determine polarity in, for example, nanowires grown in gas phase, which do not have a substrate to be used as reference for determining polarity (Heurlin et al., 2012). This technique is fast and simple and can be used on most modern TEMs. On the other hand, because an image is not obtained simultaneously, it is not straightforward to examine polarity as a function of position or, in other words, to get accurate local information. The spatial resolution is not sufficient for investigation of, for example, the polarity conversion/inversion across a twin boundary. To determine local polarity variations, other techniques are necessary.

The most direct way to determine polarity on a local level is by HAADF-STEM. Use of hardware aberration correctors on the probe-forming lens allows for the formation of a small enough beam (probe) to image atom columns individually. High-resolution HAADF-STEM images are generated from electrons scattered by the sample at high angles, which are thus incoherent and sensitive only to mass. Therefore, the two atom types making up a bilayer will have different relative intensities, allowing them to be directly identified. This technique is entirely local and therefore powerful; its use has been demonstrated for determining polarity in nanowires of InAs, GaAs, and ZnTe, to name a few (de la Mata et al., 2012; Krogstrup et al., 2009). However, to image the atoms in a bilayer directly, high microscope resolution is necessary, which limits it to the most advanced microscopes available (primarily those in which the probe-forming lenses are aberration-corrected).

High-angular annular darkfield is not suitable for analyzing light elements because the intensity of high-angle scattered electrons is too low. To analyze polarity in oxide and nitride semiconductor nanowires, annular bright field (ADF) STEM has recently been demonstrated as a powerful tool. The technique is similar to HAADF in that polarity is directly deduced from relative atomic contrast in (very) high-resolution STEM images. The only difference is that ADF uses a small ring-shaped detector to collect the direct beam disc resulting from the converged probe, rather than collecting high-angle scattered electrons. It has been demonstrated that polarity can be determined in nanowires of GaN and ZnO, both of which are difficult to analyze by other means (de la mata et al., 2012).

An additional method to determine local polarity in more conventional TEM instruments is focal series reconstruction. This technique is performed in conventional TEM mode and does not require hardware aberration correction, which means that it can be performed on a wide array of instruments. On the other hand, the technique is relatively complicated and time-consuming and requires precise knowledge of sample tilt. Normally, polarity in nanowires cannot be determined directly in high-resolution TEM images because typical nanowires are far too thick and diffraction effects complicate interpretation of the contrast. Focal series reconstruction is used to reconstruct the object wave function by recording a series of high-resolution TEM images at different focal values, and then removing the effects of image aberrations and sample thickness. It has been shown to be possible to deduce polarity across a twin boundary in InP nanowires by focal series reconstruction (Ek, Borgström, Karlsson, Hetherington, & Wallenberg, 2011).

7.2.3 Strain

High-resolution imaging of the structure of nanowires can be directly used to deduce other properties of the material. Strain in heterostructure nanowires is an example. If the composition is known (and can be independently determined by another technique), changes in the lattice parameter from high-resolution images can be used to deduce strain by geometric phase analysis of the associated Fourier transforms. In heterostructure nanowires the two materials are often well-characterized, and so local changes near their interface can be correlated with strain. This has been used to calculate strain as a function of position in Ge nanowires grown on Si and in InAs–InP heterostructure nanowires (Larsson et al., 2007; Taraci et al., 2005).

7.3 Morphology

TEM analysis normally uses electrons that have passed through a sample (transmitted), and therefore is not widely used to investigate morphology compared with scanning electron microscopy, for example. Although secondary electrons are also produced in TEM and can in principle be detected to obtain morphological images, this is uncommon and has not been applied to nanowire materials. On the other hand, the potential to obtain simultaneous morphological and structural/compositional information on a single nanowire (and in doing so, to connect morphology to structure/composition) has led some researchers to investigate the means of characterizing morphology in TEM.

The most straightforward way to measuring three-dimensional (3D) morphology directly is by electron tomography. Although it is time-consuming and relatively uncommon, this technique gives a direct 3D representation of the structure under investigation without extensive post-processing of data. Electron tomography works by tilting a sample of unknown morphology over a wide range of tilt angles (typically 80°) and reconstructing the 3D morphology from the projections. To do this, the projected image must be related to the electron beam–sample interaction by a relatively

simple relationship, which means that crystalline samples, the diffraction effects that dominate contrast in normal TEM images, are problematic. Successful electron tomography reconstruction has been obtained for semiconductor nanowires composed of a variety of materials using HAADF-STEM, because the image contrast is related only to mass and thickness. Straightforward compositional analysis can identify mass changes and simplify the distinction between mass and thickness. Electron tomography performed in the HAADF-STEM mode then gives 3D morphological images that also contain mass information and can be correlated directly to structure (Ding, Zhang, & Wang, 2013; Verheijen et al., 2007; Wu et al., 2013).

Electron tomography of semiconductor nanowires can be performed with many electron microscopes equipped with HAADF-STEM capabilities. The additional requirement is mainly that sample tilt be possible over a wide range. This requires a special sample holder but also a wide enough pole piece gap to accommodate this. In addition, software is required to perform reconstruction. In the absence of electron tomography capabilities, 3D morphology of semiconductors often can be determined by careful analysis of images obtained by conventional techniques. This is possible because of the high and well-defined symmetry of the nanowires. In particular, it is usually possible to assume that the nanowire cross-section is symmetrical, so the projected image from a low-index zone axis normal to the nanowire axis will contain equal contributions from the upper and lower sides of the nanowire (relative to the electron beam). It is often possible, for example, to deduce the cross-section directly from the intensity in HAADF-STEM images as long as compositional variations in the beam direction are not too large (Figure 7.1(e)). Because this information can easily be correlated with structure and composition for an individual nanowire, this simple analysis is surprisingly powerful.

On the other hand, semiconductor nanowires composed of a polar material may not exhibit mirror symmetry in cross-section if the structure is cubic (because a polar cubic material has only threefold symmetry in the common [111]-type growth direction). This becomes particularly problematic if the structure contains rotational defects, so that the cross-section changes along the nanowire axis. In this case, slightly more detailed analysis is needed to determine the morphology. However, the high symmetry of most semiconductor nanowires means that even in this case, it is possible to reconstruct the morphology from images taken in only a few directions and fairly simple computation (Karlsson et al., 2007).

7.4 Compositional analysis

After structure determination, compositional analysis is the most common application of TEM for the characterization of semiconductor nanowires. Several techniques widely available in TEMs can be used for fast, routine determination of the elements present in a material, and for mapping the local distribution of known elements. The most common and versatile of these is X-ray energy-dispersive spectroscopy (XEDS), in which characteristic X-rays emitted by a nanostructure are investigated to determine elements in a sample. This technique has certain limitations however,

and more precise analysis may be performed by one of several alternative techniques. The use of each of these is briefly described below.

7.4.1 X-ray energy-dispersive spectroscopy

The principle of this technique is simple: When high-energy electrons from the electron beam interact with core electrons in an atom, vacancies are created in electron orbitals. These vacancies are refilled by relaxation of electrons from higher orbitals, an event most often leading to the emission of an X-ray with energy determined by the energy spacing between electron orbitals. These are, of course, element-specific, allowing identification of elements from analysis of the emitted X-rays. XEDS can be used in combination with STEM to determine elemental composition locally and even to map the positions of specific elements in a sample (Figure 7.2). The spatial resolution is limited by sample thickness owing to beam spreading from plural scattering of electrons. Energy-dispersive X-ray detection also has limited energy resolution, much poorer than the line width of characteristic X-rays. For this reason, it is not possible to obtain more than elemental information from the detected X-rays. However, the speed and simplicity of the technique make it extremely powerful as a routine analysis tool.

XEDS analysis of semiconductor nanowire composition has been common since first reports of these structures (Hiruma, Murakoshi, Yazawa, & Katsuyama, 1996). In particular, mapping of composition is extremely important for complex semiconductor nanowires consisting of different materials in different parts of the nanowire. Axial heterostructures, in which the semiconductor material is changed along the nanowire axis, are particularly well-suited for XEDS analysis because nanowires are most easily characterized normal to their growth direction (Dick, Bolinsson, Borg, & Johansson, 2012; Krogstrup et al., 2009). On the other hand, radial heterostructures present a more complicated situation. Because the semiconductor

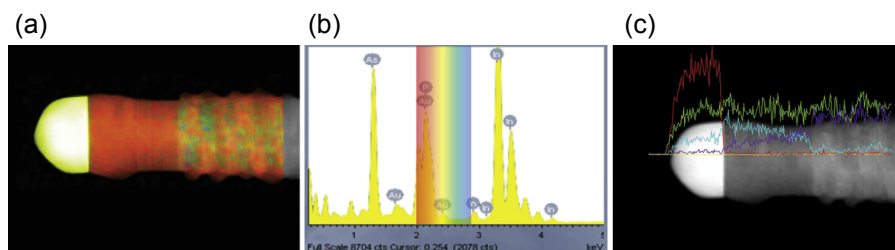


Figure 7.2 Analysis of composition by XEDS analysis. X-ray energy-dispersive spectroscopy is by far the most common routine characterization tool for nanowire composition. It is possible to extract quantitative information on elemental composition, as well as spatial information on the distribution of elements, as in (a). This map of an InAs–InP core–shell nanowire is obtained by coloring the information from the spectrum, as shown in (b). Compositional variations along the axis can be analyzed and quantified more easily using one-dimensional scans, as shown in (c), although in this case care must be taken to account for radial variations as shown here. Courtesy of S. Lehmann.

material changes in the beam direction, it is considerably more difficult to characterize the composition of all parts correctly (Todorovic et al., 2013; Venkatesan et al., 2013).

More straightforward characterization of composition in radial heterostructures and homogeneity of ternary materials can be performed with more extensive sample preparation, in particular by slicing the nanowires normal to their growth direction, as described above. For example, XEDS performed on cross-sections of GaAsSb nanowires revealed significant variation in Sb composition radially in different crystallographic direction (Conesa-Boj et al., 2014). Similarly, analysis of cross-sections of InGaP ternary nanowires revealed radial heterostructures formed simultaneously (Fakhr, Haddara, & LaPierre, 2010).

Although spatial analysis of composition can often be performed more accurately by one of several other techniques (described below), XEDS is the technique of choice when quantification of relative composition is required, because it is the only technique that allows for fast, straightforward, and accurate quantification. X-rays can be directly correlated with specific elements, and because they are not significantly absorbed by nanostructure samples, relative emission intensity is correlated only to atomic mass and the specific electron subshell. The accuracy of the quantification is limited primarily by the relatively poor energy resolution (primarily a detection problem, as described above). However, virtually no other technique can provide a comparable accuracy directly and with the high spatial precision of this technique.

7.4.2 Lattice parameter mapping

In some cases, mapping of nanowire composition can be performed more precisely by investigating the lattice parameters. This is especially useful in ternary materials or axial heterostructures, where the lattice parameter is known to fall between two fixed extreme values. The simplest means of performing this analysis is by so-called Fourier mapping, in which specific lattice spots in the Fourier transform of a high-resolution TEM image are selected to determine from where in the image they originate. This technique is useful primarily for identifying regions of nanowire heterostructures associated with two different materials that exhibit no intermixing (Björk et al., 2002; Zanolli et al., 2007). For more detailed analysis of a sample with variable composition, mapping of the lattice parameters using geometric phase analysis can be performed. This process is essentially the same as that described for mapping strain in a heterostructure nanowire. Strain mapping depends on having prior knowledge of the composition, so that the change in lattice parameter can be correlated with strain. However, if composition is unknown but strain is known, this technique can be used for accurate compositional mapping. This is reasonable in a nanowire with a graded composition, for example (Ek et al., 2013; Wallentin et al., 2013).

7.4.3 Electron energy loss spectroscopy

In some cases, the analysis techniques described above are not suitable to characterize the structure, or more information may be desired than can be deduced. In these cases,

electron energy loss spectroscopy (EELS) may be suitable. In this technique, the energy of electrons that have passed the sample is analyzed; those that have interacted with the material (by any of a variety of processes such as that producing characteristic X-rays) will have lost energy. This lost energy will be characteristic and can be used to obtain information about the sample. This has been used, for example, to analyze the different phases present in the catalyst seed particle after growth of AlGaIn nanowires (Lari et al., 2006). The spatial and energy resolution of this technique is potentially high, and detailed chemical information can in principle be obtained from fine structure in the characteristic core losses (Soumelido et al., 2013). However, it is complicated to perform EELS and it is not necessarily practical for all materials; therefore, it is not widely used to characterize semiconductor nanowires routinely. In specific cases it has proven useful for obtaining detailed information. In particular, EELS may be applied to nitride and oxide semiconductors, which are more difficult to analyze with XEDS owing to the small masses (and thus electron binding energies) of nitrogen and oxygen.

Quantification of composition can in principle be performed by EELS, and the high-energy resolution means that it can theoretically be more accurate than XEDS. However, quantification by EELS is complicated because of the much larger interaction of electrons with the sample than X-rays. The nonuniform (round or hexagonal) cross-section and moderate thickness of semiconductor nanowires means that they are not well-suited to this type of analysis, and reports are scarce (Heiss et al., 2011).

However, analysis of nanowire properties by EELS is not limited to determining composition by core-loss energies (so-called edges). The EEL spectrum also contains electrons that have undergone other lower-energy interactions with the sample, such as plasmon oscillations. The low-energy EEL spectrum is complex and difficult to analyze directly, but is characteristic for a material and can be compared with spectra from known materials to identify composition. Finally, the low-loss region of an EEL spectrum contains more than just compositional information. For example, onset of the low-loss region indicates the band gap, and detailed analysis of this region can give detailed electronic information. This has been used, for example, to investigate GaIn nanowires containing sections of cubic and hexagonal stacking, which have different electronic structures (Arbiol et al., 2009).

7.4.4 High-angular annual darkfield scanning TEM compositional analysis

Finally, it is possible to obtain detailed composition information by careful analysis of HAADF-STEM images. This technique is sensitive to mass and can in principle be used to obtain atomically resolved images in microscopes with high resolution. Detailed analysis by this technique is thus a powerful way to obtain compositional information with atomic resolution from the relative intensity of different atom types. Because no absolute chemical information is obtained, this technique depends on the prior identification of atoms present in a sample, and must therefore be combined with other analysis techniques or with well-defined materials. However, this technique has been used successfully to quantify composition in nanowires containing regions of

known composition to calibrate intensity (such as heterostructure nanowires containing ternary segments or interfacial grading) (Kauko et al., 2013; Todorovic et al., 2013).

Polarity determination by HAADF-STEM as described above can be thought of as a special case of compositional analysis using this technique. However, in the former case the identities of the atom types were known and they were assumed to be arranged regularly in the lattice—only their relative positions were under investigation. For this reason, the analysis was described as structural rather than compositional. The major strength of HAADF is, of course, the extremely high resolution: Although compositional techniques such as XEDS and EELS can in principle be performed with atomic column resolution in an aberration-correct STEM, they are still some way from locating individual atoms. High-angular annual darkfield scanning TEM has been used to locate individual gold atoms in both Si and GaAs nanowires (Allen et al., 2008; Bar-Sadan, Barthel, Shtrikman, & Houben, 2012). By comparing HAADF signal intensities with simulations at different (slightly off-axis) tilts, it was even shown that the position of Au atoms within the semiconductor nanowire atomic column can be determined.

7.5 *In situ* analysis of properties

One exciting possibility in modern TEMs is investigating the response of semiconductor nanowires to changes induced while simultaneously imaging (Petkov, 2013). This may include the response of the nanowire to temperature changes, electrical current, or mechanical force. It also includes nanowires grown under TEM imaging by introducing gases into environmental TEM.

7.5.1 *Mechanical properties*

Mechanical properties of nanowires can be determined in TEM in a variety of ways. One of the simplest types of setup consists of some type of probe integrated with the sample holder, which can be manipulated to push against a nanowire extending into the field of view. By applying stress to the nanowire, its behavior under force can be deduced. Simultaneous TEM imaging is then used to perform the experiment more easily (contacting two fine tips is much easier when they are visible) and to determine the extent to which the nanowire is deflected for a given applied force. An important point is to relate the exact deformation of the nanowire to the applied stress, which requires accurate knowledge of the cross-sectional area of the specific nanowire under investigation. When comparing elastic properties of different nanowires, local information on structure and especially defects is particular. For many types of measurements, fast recording time is also an asset. For these reasons, *in situ* TEM is superior to many other techniques used to deduce mechanical properties (Asthana et al., 2011; Kizuka, Takatani, Asaka, & Yoshizaki, 2005).

More advanced setups are based on micro-electromechanical systems (MEMS) devices. TEM holders designed to accommodate MEMS chips are becoming more common and have a significant advantage in that the functionality can be

modified with the removable part, which means that the holder itself can accommodate a broad array of functions. The use of MEMS devices for mechanical testing of semiconductor nanowires has been demonstrated in a few instances (Agrawal, Peng, Gdoutos, & Espinosa, 2008). Other techniques measure mechanical properties by inducing resonances with an applied voltage and extracting elastic properties from the resulting deflection amplitude (Huang, Bai, & Zhang, 2006), or by inducing bending in the TEM support grid to cause subsequent bending in the nanowire (Han et al., 2007). In all cases, mechanical properties can be extracted and directly correlated with the local structure for a wide variety of semiconductor nanowire materials.

7.5.2 Electrical measurements

Simple electrical measurements of nanowire properties can be performed using means similar to those used to measure mechanical properties. For example, if the moveable probe is conducting, it can in principle be used as a contact for analyzing electrical properties. This has been demonstrated, for example, for InAs nanowires (Larsson, Wallenberg, Persson, & Samuelson, 2004) using purpose-built TEM-STM holders, which include an integrated conducting probe on a TEM holder. This put certain limits on the sample geometry and the measurements are by default simplified, but it can give important insights into the relationship between individual nanowire structural and compositional properties and the resulting electrical conductivity.

More advanced setups, as for mechanical characterization, can be based on MEMS devices. Because the devices can be customized, the possible functionality is wide and use of this geometry may become more widespread in the future. To date, there have been several demonstrations of the potential for this type of investigation (Espinosa, Rodrigo Bernal, & Filleter, 2012). In another example, *in situ* nanowire growth (see Section 7.5.4) was performed on a prefabricated Si device specially developed for electrical characterization of nanowires. By fabricating the nanowires directly within the device, more complex device geometry could be used and therefore more detailed measurements were possible (Kallesoe et al., 2012).

7.5.3 Heating experiments

The possibility of heating samples directly in electron microscopy has been available for many years, and local heaters fit to sample holders are relatively widely available. In recent years, these heaters have advanced from furnace type to spiral type, and most recently to MEM-based local heating. A variety of experiments have been conducted on semiconductor nanowires that give important insights into the properties and processes relevant to their fabrication.

The simplest experiments consist of heating a nanowire viewed in a known direction in a vacuum and watching how it responds to the temperature change (see Figure 7.3(a) and (b) for an illustration). Even such conceptually simple experiments can give profound insights into the materials and the processes affecting them. As an example, *in situ* heating experiments have been used to investigate the phase of the

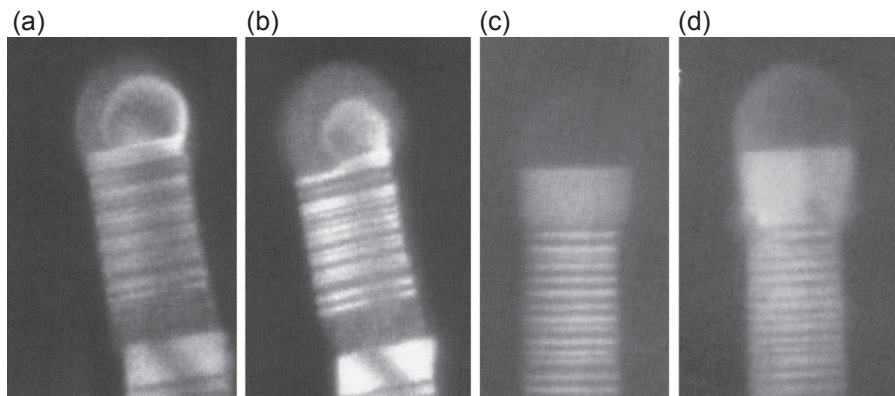


Figure 7.3 *In situ* experiments conducted in TEM. (a,b) *In situ* heating experiments can give insight into the stability of the nanowires and their seed particles under a variety of relevant conditions, which may include vacuum and suitable atmospheres. Here, the phase change of the catalyst particle on a GaAs nanowire is investigated as it is heated. (c,d) By introducing relevant precursor gases at suitable temperatures, nanowires can also be grown inside a TEM, giving substantial insight into the growth kinetics. Here, this is shown for a GaAs–Ge heterostructure nanowire.

catalyst seed particle under temperatures comparable to nanowire growth, leading to the important hypothesis that this particle may be solid (rather than previously accepted liquid) during growth of standard semiconductor materials (Persson et al., 2004). Other experiments have been used to investigate the stability of nanowire material at elevated temperatures, which is especially important for determining the technological limits of applications of these materials. For example, InAs (Pennington et al., 2010), CdTe, and ZnTe (Davami et al., 2011) all have been observed to decompose at unexpectedly low temperatures when during *in situ* TEM heating studies.

Other processes such as phase changes have been investigated by *in situ* heating experiments. For example, numerous studies have been performed in the formation of silicides and germanides from Si and Ge nanowires in contact with specific metals (Chou et al., 2008; Lu et al., 2007).

7.5.4 *In situ* nanowire growth

The most complex type of *in situ* TEM experiments involves the introduction of semiconductor precursor gases into the TEM, to watch the nanowires in real time as they grow (Figure 7.3(c) and (d)). Experiments of this type have been performed in several instruments worldwide with environmental capabilities, which means that they have been modified to allow for significantly higher pressures in the sample region than at the electron gun (which requires a high vacuum). This is achieved primarily with additional pumping capacity and differential apertures in the sample region. Most investigations have been performed on Si and Ge nanowires grown using the precursor gases disilane and digermane (Hannon, Kodambaka, Ross, & Tromp, 2006; Hofmann

et al., 2008; Kodambaka, Tersoff, Reuter, & Ross, 2007). Several investigations have focused on other materials including GaN, GaP, and GaAs (Chou et al., 2014; Diaz et al., 2012).

Although by necessity nanowire growth experiments performed in a TEM take place under conditions different from normal growth, they have nevertheless provided numerous important insights that have broadly changed the understanding of nanowire growth and properties. Important insights have, for instance, been gained in the action of the catalyst particle, giving information on the stability (Hannon et al., 2006) and phase (Hofmann et al., 2008; Kodambaka, 2007) that could not be directly deduced from room temperature post-growth experiments. In particular, *in situ* experiments definitely answered questions regarding the state of the particle (solid or liquid), directly proving that both states can occur depending on conditions. *In situ* growth experiments also gave important input into the development of heterostructure nanowires, demonstrating controlled *in situ* changes in the state and composition of the catalyst particle as a pathway to achieving much improved heterostructure interfaces.

The most dramatic insights obtained concern the dynamic nature of the particle—nanowire interface during growth. Specifically, authors in three different groups noted the appearance of oscillating corner facets at the outer edge of the interface (Gamalski, Ducati, & Hofmann, 2011; Oh et al., 2010; Wen et al., 2011). Existing growth models assumed the formation of sequential flat layers after nucleation at the edge, and so the observation that the interface morphology is continuously changing (demonstrated for Si, Ge, GaP, and even Al_2O_3) has caused significant interest and changed the fundamental understanding of the nanowire growth process.

7.6 Summary and outlook

The use of TEM to characterize semiconductor nanowires has been widespread for as long as nanowires have been fabricated. The technique is routinely used to characterize structure and composition, but also for more advanced analysis of a wide variety of properties including polarity, strain, morphology, and electronic structure, to name a few. The availability of significantly more advanced TEM-based characterization techniques has expanded greatly in recent years, and with it the possibility for application to nanowire structures. In particular, the development of hardware aberration correctors has had a tremendous impact, especially on HAADF-STEM, which is rapidly developing into being the most important tool for characterizing material properties of semiconductor nanowires.

The use of *in situ* analysis techniques to measure a variety of other properties while simultaneously imaging in TEM is also a rapidly expanding field. Although the number of reports is still relatively new owing to the complex nature of the experiments and significant hardware demands, new and better methods are being developed continuously and a much broader impact can be foreseen in the future. Even today, *in situ* measurements have a considerable impact on the development of semiconductor nanowire materials.

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Electron holography of nanowires — Part 1

8

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8.1 Application details

For more information about introduction to electron holography, please refer to the chapter prepared by Dr den Hertog (Ch.9). In this section, characterization of hole accumulation in core/shell nanowires (NWs) (Li et al., 2011), polarization fields across polytype interfaces in II–VI (Li et al., 2012) and III–V semiconductor NWs (Li et al., 2013), active dopants, and electrostatic potentials within *in situ* biased NWs are presented (Cumings, Zettl, McCartney, & Spence, 2002; Gan et al., 2013; He, Cho, Jung, Picraux, & Cumings, 2013), which may attract interest of both experts in electron holography and possibly a larger readership interested in semiconductor NWs for numerous applications.

8.1.1 Hole accumulation in Ge/Si core/shell nanowires

The Ge/Si core/shell system has a staggered Type-II band lineup, with a valence band offset of several hundred meV between the Ge core and the Si shell (Schäffler, 1997). Thus, the holes are expected to reside in Ge, which has been proven both theoretically and experimentally in Ge quantum dots embedded in a Si matrix (Li, Ketharanathan, Drucker, & McCartney, 2009; Seok & Kim, 2001). It has been reported that field-effect transistors (FETs) incorporating i-Ge/i-Si core/shell NWs exhibit substantial current at zero gate voltage ($V_g = 0$), validating their behavior as p-type depletion-mode FETs (Lu, Xiang, Timko, Wu, & Lieber, 2005; Xiang et al., 2006). The direct detection of holes in Ge/Si core/shell NWs through enhanced Raman scattering has also been reported (Zhang, Lopez, Hyun, & Lauhon, 2010). This current study focuses on direct observation of static charge accumulation inside individual core/shell NWs using off-axis electron holography, and calculations of the corresponding charge densities.

Epitaxial $\langle 110 \rangle$ -orientated Ge/Si core/shell NWs were grown on Si (111) substrates following the vapor–liquid–solid (VLS) growth mode (Dailey & Drucker, 2009). The seed particles are presumed to have been dislodged during heating of the Ge cores before growth of the Si shells, and no seed particles were observed on the final Ge/Si core/shell NWs.

In the following, the high-resolution electron microscopy (HREM), energy-dispersive X-ray spectroscopy (EDS), and off-axis electron holography observations were carried out using a Philips CM200-FEG transmission electron microscope (TEM) equipped with an electrostatic biprism and a $2.8 \text{ k} \times 2.6 \text{ k}$ Gatan Orius

SC200W charge-coupled-device camera. The off-axis electron holography was set up in the normal TEM geometry with a biprism voltage of ~ 130 V and a fringe contrast of $\sim 60\%$ in vacuum. High-angle annular-dark-field (HAADF) images were obtained using a JEOL 2010F electron microscope. The electron holography analysis was performed first, followed by plasma cleaning of the sample for a few seconds, and then the scanning transmission electron microscopy (STEM) intensity data were obtained from the same NW. This approach allowed a clean sample for electron holography before any damage or contamination was caused by the focused electron beam used for STEM analysis.

Figure 8.1(a) is an HREM image of a Ge/Si core/shell NW viewed along $\langle 111 \rangle$ zone axis. Both the Ge core of darker contrast (~ 10 nm) and the Si shell regions are generally of good crystallinity. The HAADF image of another Ge/Si core/shell

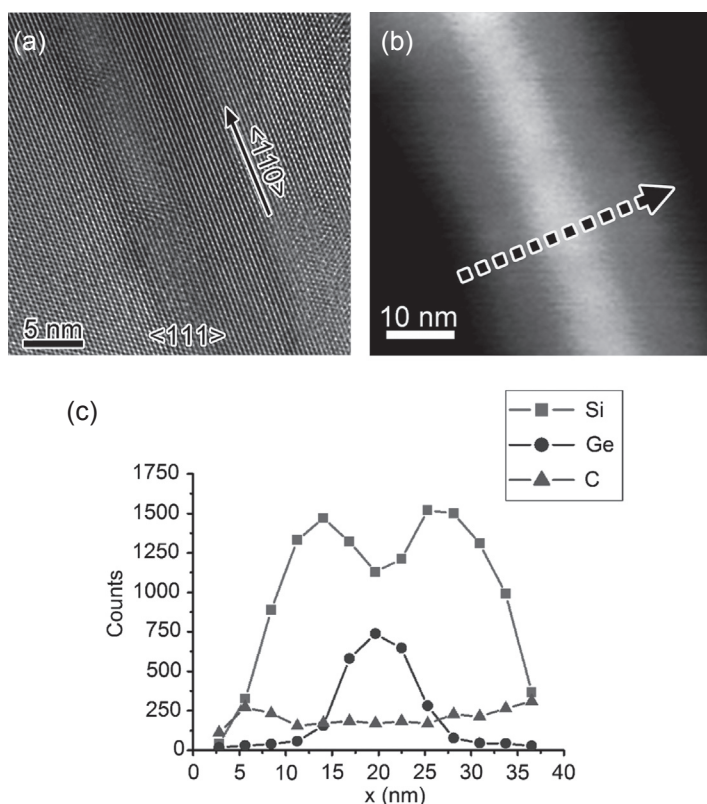


Figure 8.1 (a) HREM image of a specific Ge/Si core/shell NW with good crystal quality projected along $\langle 111 \rangle$ direction, and the growth direction is along $\langle 110 \rangle$. (b) HAADF image of another Ge/Si core/shell NW showing brighter contrast in the core region. The dashed arrow indicates the region for EDS line profiles. (c) EDS line profiles: line with squares is for Si, line with disks is for Ge, and line with triangles is for C.

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NW (Figure 8.1(b)) shows brighter contrast in the Ge core region as expected, and the corresponding EDS line profiles (Figure 8.1(c)) across the region indicated by the dashed black arrow in Figure 8.1(b) confirms the compositional structure of the core/shell NWs.

To use phase changes measured by off-axis electron holography to determine whether charge accumulation is present in Ge/Si core/shell NWs, it is necessary to accurately measure contributions to the electron phase shifts due to the projected thicknesses for both the Ge core and the Si shell. Since the step size (2.8 nm for our case) used for EDS line profile analysis is too large to allow accurate determination of projected thicknesses, intensity profiles from HAADF images with much smaller step size are utilized for this purpose.

HAADF images were obtained with a spot size of ~ 0.2 nm. The region outlined in the box in Figure 8.2(a) was used for the following electron holography analysis. The dashed arrow shows the region selected for intensity line profile, as presented in Figure 8.2(b). The white circles are the experimental data with a step size of 0.19 nm, which is more than an order of magnitude smaller than the step size used previously for EDS analysis. To reduce the noise level, both the core and the shell regions were fitted with polynomials; the latter is extrapolated to the core region to emphasize the different contributions of Ge and Si to the image intensity.

The HAADF intensity is proportional to projected sample thickness via the factor Z^α , where Z is the atomic number, and the exponent α should have a value between 1 and 2 depending on microscope geometry (Hartel, Rose, & Dinges, 1996). The width of the Ge core region for this specific NW is 8.7 nm, and the overall width of the Ge/Si core/shell NW is 25.7 nm, as obtained from the corresponding HREM image. We assume that the central projected thicknesses for the core and the whole NW have the same value s as the measured widths of the core and the whole NW, and the exponent α is calculated to be 1.5. This value of α was then used for calculation of the projected thicknesses of the Ge core and the Si shell separately across the NW, as shown in Figure 8.2(c). (Determination of the exponent α , and calculations for Ge and Si projected thicknesses, are described in the Supporting Information of Li et al., 2011.)

Figure 8.3(a) and (b) are hologram and corresponding reconstructed phase image of the same NW. The dashed arrow in Figure 8.3(b) indicates the region used for phase-shift line profile analysis, which is the same region used for the HAADF intensity line profile. The result is represented by squares in Figure 8.3(c) and fitted with polynomials to lower the noise level. The triangles show the calculated phase shift across the NW using the projected thickness data obtained from the HAADF intensity line profile. Mean inner potential (MIP) values of 15.5 V for Ge and 12.0 V for Si were used to calculate the expected phase shifts according to the projected thicknesses, which are close to the experimental phase shifts in the shell region but are much reduced relative to the experimental data in the core region.

The MIP values for nanostructures might be anticipated to be different from their bulk values because of the large proportion of surface atoms (Popescu, Müller, Wanner, & Gerthsen, 2007). For example, Chung and Rabenberg (2006) reported the MIP of Ge to be 15.5 V based on electron holographic measurements of Ge NWs

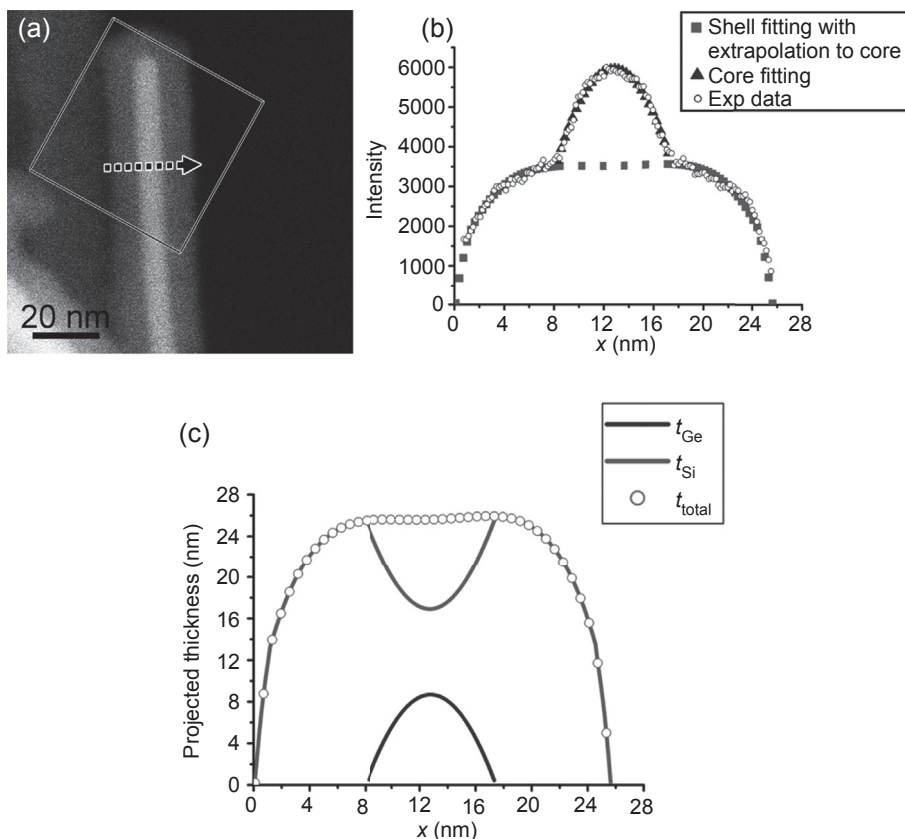


Figure 8.2 (a) HAADF image of a Ge/Si core/shell NW with the region used for intensity line profile analysis labeled by dashed arrow. The region in the box is what is used for the following electron holography analysis. (b) Intensity line profile across the NW shown by white circles. The core region (triangles) and shell region (squares) are fitted with polynomials, and the latter is extrapolated to the core region to emphasize the different contributions of Ge and Si to the image intensity. (c) Calculated projected thicknesses for Ge core (dark line), Si shell (light line). The overall projected thickness is presented by white circles.

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of diameter ~ 110 nm with oxide shells, whereas [Li, McCartney, Dunin-Borkowski, and Smith \(1999\)](#) reported MIP of Ge to be 14.3(2) V for a cleaved Ge wedge. For our core/shell NW system, the Ge cores are embedded inside Si shells, meaning that the cores are likely to be compressed ([Goldthorpe, Marshall, & McIntyre, 2008](#)), so that a higher MIP than for bulk material might reasonably be expected. Thus, 14.3 V was taken as the lower boundary value for the MIP of Ge in our experiments.

The differences between the experimental and calculated phase shifts based on projected thicknesses applying two different MIP values of Ge are presented as squares and triangles in [Figure 8.3\(d\)](#). The positive phase differences between the experimental

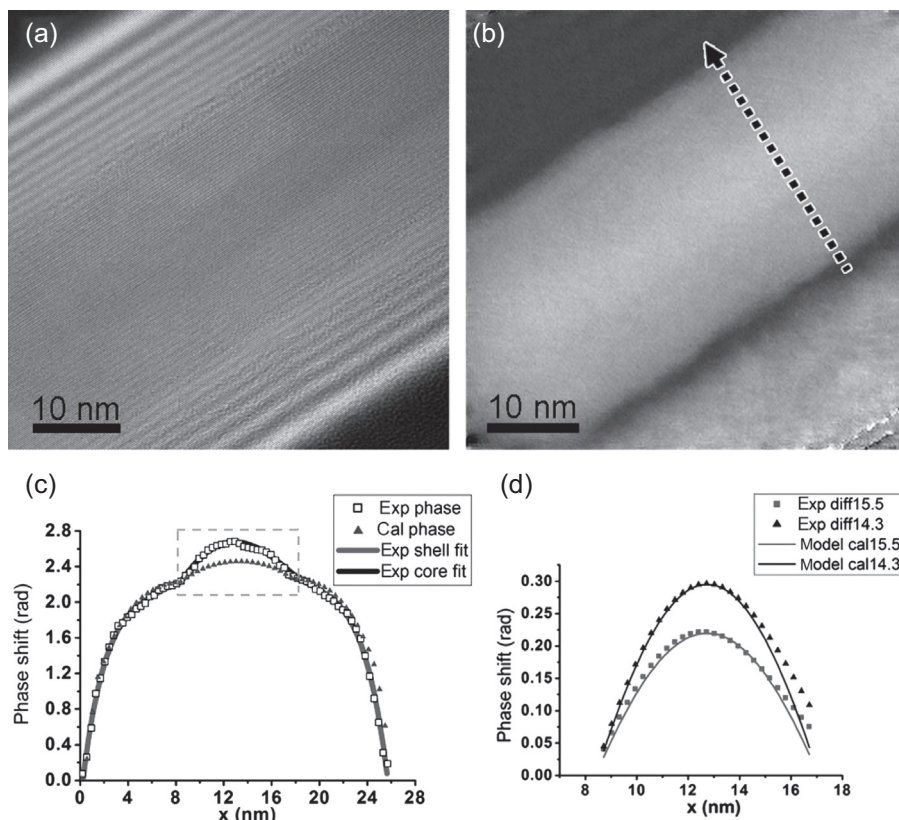


Figure 8.3 (a) Electron hologram of the same NW observed by HAADF. (b) Reconstructed phase shift image of the NW, with the region used for HAADF intensity line profile labeled with dashed arrow for phase shift profile. (c) The experimental phase shift profile is shown by white squares; the triangles are calculated phase shifts using the projected thicknesses obtained from HAADF intensities. Both profiles are fitted with polynomials to lower the random noise level. (d) The differences between experimental and calculated phase shifts across the NW. Mean inner potential values of 15.5 V (squares) and 14.3 V (triangles) for Ge, and 12.0 V for Si were used in the calculations. The dark and light lines are corresponding excess phase shifts calculated based on the coaxial cylindrical model. Reprinted with permission from [Li et al. \(2011\)](#). Copyright (2011) American Chemical Society.

and expected phase shifts due to thicknesses would seem to indicate possible accumulation of holes in the core region. The lower Ge MIP value results in slightly larger excess phase shifts in the core region.

It is reasonable to expect hole accumulation in the Ge core and negative charges in the surface regions of the shell due to the large valence band offsets between Ge core and Si shell. The presence of negative charge in the surface oxide has been reported for n-type doped single Si NWs ([Hertog et al., 2009](#)). For our case, the origin of these negative charges could be either ionized surface states or adventitious ionized surface

dopants. To estimate the hole density in the core, for simplicity our analysis assumed the coaxial cylindrical core/shell model, and that charge densities in the core and surface oxide regions were uniform. Applying Gauss's law to the core and shell regions separately, the projected electrostatic potential is obtained, which can then be converted into a phase shift. The calculated excess phase shifts are presented in Figure 8.3(d), which include scaling factors appropriate for the two different MIP values for Ge. When 15.5 V is used for the MIP of Ge, the hole density is calculated to be $0.5/\text{nm}^3$, whereas the hole density is $0.6/\text{nm}^3$ when 14.3 V is used. (Details of these calculations of projection of potential and hole density are given in the Supporting Information of Li et al., 2011.)

This approach of combining measurements from HAADF and electron holography observations has been applied to several other Ge/Si core/shell NWs. For those NWs having core diameter of ~ 10 nm, the differences between experimental and calculated phase shifts show similar excess positive phase shifts in the core, and an average hole density of $(0.4 \pm 0.2)/\text{nm}^3$ is obtained. However, for NWs with considerably smaller core diameters (~ 6 nm), it is interesting that the differences do not show the excess positive phase shift in the Ge core.

Estimation of hole densities inside Ge/Si core/shell NWs can also be made based on published measurements. The differential conductance G for Ge/Si core/shell NWs of core diameter ~ 10 nm and length ~ 170 nm has been found to be of the order of $\sim 2e^2/h^4$, and the corresponding conductivity σ is calculated to be $\sim 1.67 \times 10^{-4}$ C/V s nm. The hole mobility for back-gate Ge NW transistors of diameter ~ 20 nm has also been measured as a function of V_g (Wang et al., 2003). When $V_g = 0$ V (which corresponds to the experimental condition for the current work), the hole mobility is ~ 70 $\text{cm}^2/\text{V s}$, and the corresponding hole density is calculated to be $\sim 0.2/\text{nm}^3$ applying the relation $n = \sigma/e\mu$. Here n represents hole density, σ is conductivity, and μ is hole mobility. The estimated value is in reasonable agreement with hole density reported here.

8.1.2 Polarization-induced charge distribution at polytype interfaces in semiconductor nanowires

Tailoring of charge distribution has been a hot topic for semiconductor-based materials ever since the discovery of Si p–n junctions in the 1940s (Michael & Hoddeson, 1988). Heterojunctions consisting of materials with different bandgaps exhibit considerable valence and/or conduction band offsets at the interfaces, which cause electrons or holes to reside in the same material (Drexler, Leonard, Hansen, Kotthaus, & Petroff, 1994) (type I band alignment) or become separated in different materials (Li et al., 2011; Lu et al., 2005) (type II band alignment).

Heterocrystalline polytype structures have been intensively studied in recent years as novel types of superlattices, which consist of chemically identical but structurally different materials and match well at their interfaces (Bechstedt & Käckell, 1995). Thus, the common problem of compositional changes associated with interfaces composed of chemically inequivalent materials can be avoided. The basic polytype structures for III–V and II–VI compounds are zincblende (ZB) with cubic stacking

in the [111] direction and wurtzite (WZ) with hexagonal stacking in the [0001] direction. The controlled growth of polytypic and twinning superlattices, which is rare in related bulk crystals, has been realized in single NWs by varying the NW diameter and growth temperature (Caroff et al., 2009), by the addition of dopants (Algra et al., 2008; Xu et al., 2012) and by varying the group V partial pressure during growth (Spirkoska et al., 2009). Here we demonstrate that the growth of homogeneous WZ/ZB heterostructural junctions in compound semiconductors represents a viable alternative approach to achieving tailoring charge distribution at the nanoscale.

The WZ structure is expected to possess intrinsic spontaneous polarization (SP) since the four tetrahedral bonds do not have equivalent bond-to-bond charge transfer and ionic relaxation can introduce SP along the (*c*-axis) stacking direction (Qteish, Heine, & Needs, 1992). Conversely, the tetrahedral bonds are symmetric for the ZB structure. Thus, the cubic ZB structure has no bulk SP when grown along $\langle 111 \rangle$.

8.1.2.1 Homogeneous ZB/WZ heterostructural junctions in ZnSe nanobelts

The homogeneous ZB/WZ ZnSe heterostructural junctions were fabricated via thermal evaporation of ZnSe powder (Jin et al., 2010). The off-axis electron holography observation and HREM imaging were carried out using a Philips CM200-FEG TEM. The sample was imaged in the diffraction mode but with the diffraction lens turned off in order to obtain a larger field of view. The interface fringe spacing was ~ 0.57 nm, and the overall image magnification was set at ~ 120 kX. The HREM images used for strain-map calculations were obtained using a JEOL JEM-2010 FEF (UHR) TEM. The aberration-corrected imaging was performed in the HAADF mode using a JEOL ARM200F TEM. All microscopes were operated at an acceleration voltage of 200 kV.

An atomic model for the WZ/ZB/WZ interfaces is presented in Figure 8.4a. Due to the asymmetric tetrahedral bonding in the WZ unit cell, dipoles should accumulate along the [000–1] direction, leaving positive charges at the WZ/ZB junction and negative charges at the ZB/WZ junction. Thus, there should be linearly increasing electrostatic potential in the WZ region, and linearly decreasing electrostatic potential in the ZB region, induced by those polarization charges, as shown in Figure 8.4(b). Theoretical calculations of potential profiles across the interfaces and charge densities at the junctions have been previously reported (Posternak, Baldereschi, Catellani, & Resta, 1990; Qteish et al., 1992), which show the same saw-tooth-like features as sketched in Figure 8.4(b).

The atomic arrangements and polarity continuity at the ZB/WZ interface of a specific ZnSe nanobelt was determined using aberration-corrected HAADF imaging, as shown in Figure 8.4(c) (right). The left region is projected along $[\bar{1}10]_{\text{ZB}}$, while the right region is projected along $[\bar{2}110]_{\text{WZ}}$. The intensity line profiles along an array of Zn–Se atomic columns in the ZB region, and dumbbells in two directions in the WZ region are shown on the left, which indicates that the crystal polarity maintains the same direction across the ZB/WZ interface. Consequently, no charge accumulation due to polarity reversal would be anticipated at the interface.

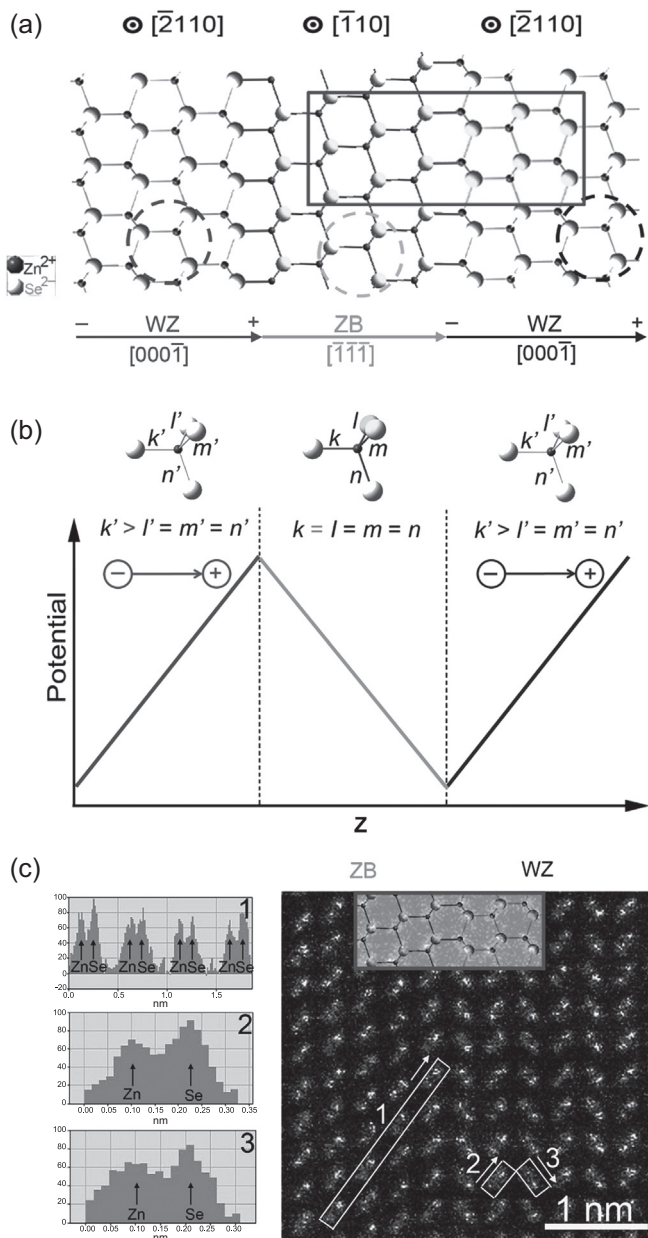


Figure 8.4 (a) Atomic model for the WZ/ZB/WZ heterostructures projected along $[\bar{1}10]_{\text{ZB}}$ and $[\bar{2}110]_{\text{WZ}}$, with $[1\bar{1}\bar{1}]_{\text{ZB}}$ parallel to $[000\bar{1}]_{\text{WZ}}$ along the interface normal. (b) Sketch of the saw-tooth-like potential profile. (c) (Right) Aberration-corrected HAADF image of ZB/WZ interface with individual Zn–Se atomic columns clearly resolved. The region in the box in (a) is overlapped, which fits well with the experimental interface structures. (Left) The intensity line profiles on both sides of the interface confirm polarity continuity across the interface.

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Figure 8.5(a) shows an off-axis electron hologram of a ZnSe nanobelt including WZ/ZB/WZ junctions. The nanobelt was first tilted to the closest $[\bar{1}10]_{\text{ZB}}/[2110]_{\text{WZ}}$ zone axis and then rotated slightly about the axis normal to the junctions $[111]_{\text{ZB}}/[0001]_{\text{WZ}}$ in order to avoid diffraction contrast while the junctions were kept edge-on. Figure 8.5(b) presents an HREM image of the same nanobelt, with the bottom left corner corresponding to the amorphous layer along the edge of the nanobelt. There is a WZ region of width ~ 7 nm to the right of the amorphous layer, followed by a ZB region of width ~ 22 nm, and a wider region of WZ that is only partly visible in the HREM image.

Figure 8.5(c) and (d) are the corresponding reconstructed phase and thickness images, respectively. The thickness image was calculated based on the reconstructed amplitude image assuming a value of 67 nm (GaAs) (Chung, Smith, & McCartney, 2007) for the inelastic mean free path (MFP) for ZnSe (McCartney & Gajdardziska-Josifovska, 1994). The MFP value for ZnSe was unknown. However, it was reasonable to employ the MFP of GaAs since ZnSe and GaAs have equal average atomic numbers, which is the primary factor in determining the magnitude of the inelastic MFP.

Line profiles for the phase shift and thickness perpendicular to the WZ/ZB/WZ junctions are shown in Figure 8.5(e) and (f), respectively. The box region used for line profiling is outlined in Figure 8.5(c) and (d), starting from the interface of the amorphous layer and the bottom WZ region. The phase shifts in Figure 8.5(e) increase almost linearly in the WZ region and decrease linearly in the ZB region, while the turning points coincide with the junction positions. The thickness profile, on the other hand, is flat across the entire region, which implies that the thickness is effectively constant. Thereby, the observed saw-tooth-like phase shifts indicate that opposing electrostatic fields are present in the ZB and WZ regions, so that charges of opposite signs must be located at these junctions.

The choice of ZnSe is critical for this investigation since ZB/WZ interfaces in ZnSe nanobelt have been calculated to have close to zero valence and conduction band offsets (Akiyama, Yamashita, Nakamura, & Ito, 2010). Thus, the possibility of charge separations due to band offsets (Spirkoska et al., 2009) could be precluded, making it possible to measure the SP-related electrostatic field separate from any other charge redistribution mechanism.

For nitride-based heterostructures, the electrostatic potential across junctions is usually induced by the combination of both SP and piezoelectric polarization (PE). Thus, it is necessary to take possible contributions from PE into consideration in our experiment. Figure 8.6(a) is an HREM image showing the ZB/WZ interface of another ZnSe nanobelt. The geometric phase analysis (GPA) procedure for mapping displacement fields and strain fields from HREM images was utilized (Hýtch, Snoeck, & Kilaas, 1998). Meanwhile, a GPA program compatible with digital micrograph was applied for calculation of the strain map.

Figure 8.6(b) shows the strain map for ε_{zz} , which is the normal strain component along the z direction, that is, $[111]_{\text{ZB}}/[0001]_{\text{WZ}}$, whereas the reference lattice was taken from the ZB region. The corresponding line profile across the ZB/WZ interface is presented in Figure 8.6(c). The value of ε_{zz} away from the interface is approximately zero, whereas the normal strain component across a strained heterostructured interface

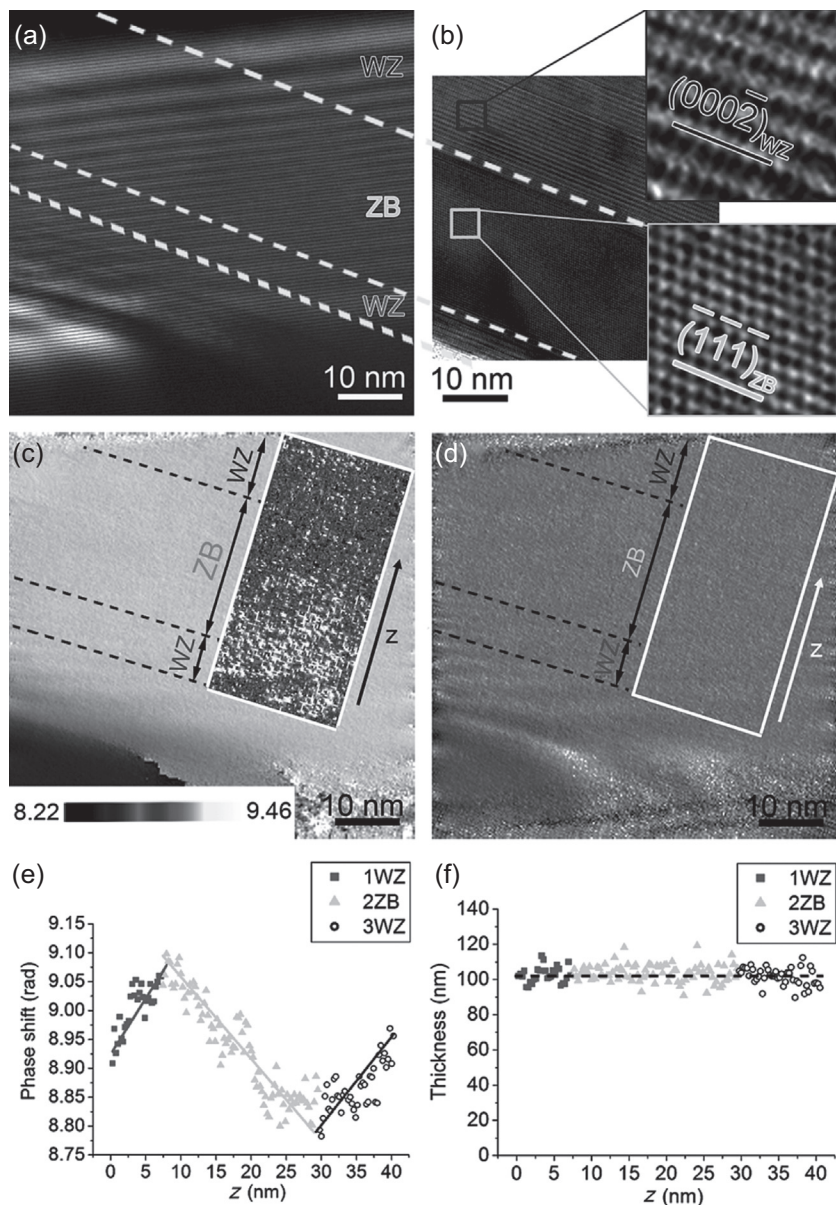


Figure 8.5 (a) Electron hologram from region including WZ/ZB/WZ heterostructural junctions. (b) HREM image of the same nanobelt projected along $[\bar{1}10]_{\text{ZB}}/[\bar{2}110]_{\text{WZ}}$ zone axis. Part of the ZB and WZ regions are enlarged to clearly show the lattices. (c) Reconstructed phase shift with the boxed region used for profiling. (d) Thickness image of the same region with the ZB and WZ regions labeled. (e) Phase shifts of the box region labeled in (c). (f) Thickness profile of the box region labeled in (d), which is the same region used for phase shift profiling.

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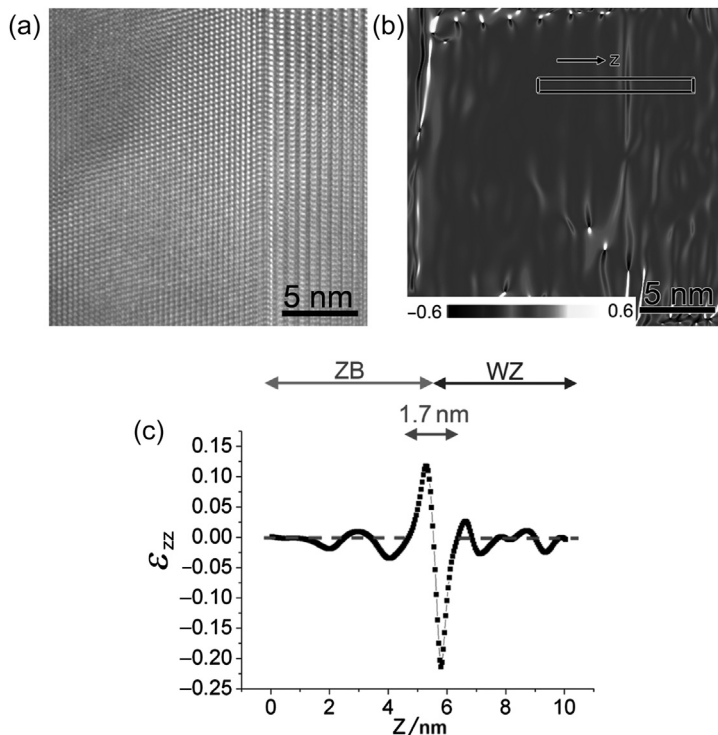


Figure 8.6 (a) HREM image of ZB/WZ interface. (b) Strain map for the normal component ϵ_{zz} of the same region of HREM imaging. (c) Line profile of ϵ_{zz} of the box region labeled in (b).

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should normally give a step-like profile (Hýtch et al., 1998; Hüe, Hýtch, Houdellier, Snoeck, & Claverie, 2008). Thus, the close-to-zero values in the ZB and WZ regions away from the immediate vicinity of the interface indicate extremely low levels of strain in both regions, and hence negligible PE contributions to the observed electrostatic fields. The sharp abrupt peaks visible at the interface may result from phase shifts that originate from the deviation from periodic translational symmetry of the crystal lattices across the interface or possible slight local tilt.

Since ϵ_{zz} is approximately zero away from the interface, the long-range linear slopes visible in Figure 8.5(e) must be mainly induced by SP present in the WZ regions. The phase shift profile in Figure 8.5(e) can be converted to electrostatic potential using: $\varphi = C_E (V_{\text{MIP}} + V_{\text{SP}}) t$, where V_{MIP} is the MIP of the material, and V_{SP} is the SP-related electrostatic potential. Only the latter term would contribute to the electrostatic fields as a slope of the electrostatic potential profile since the MIP is constant for a specific structure. Thus, the electrostatic field E can be calculated for both ZB and WZ regions based on a linear fit of the experimental phase shift data: $E_{\text{ZB}} = 0.0189$ V/nm, $E_{\text{WZ}} = -0.0204$ V/nm.

The SP in the WZ region can be calculated using (Qteish et al., 1992; Bernadini, Fiorentini, & Vanderbilt, 1997):

$$p_{\text{sp}} = -\epsilon_0 \epsilon_r \Delta E = -\epsilon_0 \epsilon_r \left(\frac{\partial V_{\text{WZ}}}{\partial z} - \frac{\partial V_{\text{ZB}}}{\partial z} \right) \quad (8.1)$$

where $E_{\text{WZ}} = -\frac{\partial V_{\text{WZ}}}{\partial z}$ and $E_{\text{ZB}} = -\frac{\partial V_{\text{ZB}}}{\partial z}$ correspond to the electric fields in the WZ and ZB regions and $\epsilon_r = 9.25$ (at $T = 296$ K) is used (Strzalkowski, Joshi, & Crowell, 1976). Thus, the SP present in the WZ region is estimated to be $p_{\text{sp}} = -0.0032 \pm 0.00014$ C/m².

Since no calculated or experimental SP values are available for ZnSe, the bulk SP value for WZ-ZnSe and ZB-ZnSe are calculated using the Berry phase expression (King-Smith & Vanderbilt, 1993; Resta, 1994) based on first-principles calculations implemented in VASP (Kresse & Furthmüller, 1996a, 1996b), as well as the supercell approach (Qteish et al., 1992). The bulk SP values calculated using the so-called Berry phase approach are -0.0063 and 0.0 C/m², for WZ-ZnSe and ZB-ZnSe, respectively. The calculated SP value for WZ-ZnSe employing the ZB-ZnSe/WZ-ZnSe supercell is -0.0022 C/m².

Since the SP value calculated by Berry phase approach provides an intrinsic value for ideal bulk WZ-ZnSe crystal, and taking into account the possible lowering effect from finite nanoscale system and possible defects in the nanobelts, the calculated value would provide an upper limit; the SP value obtained from the supercell approach, where the supercell is constructed with two ZB unit cells and two WZ unit cells through modeling of the experimental ZB/WZ heterostructural junction, could be considered as a lower limit. Our experimental SP value falls reasonably within the range of theoretical calculations ($0.0022 < 0.0032 < 0.0063$ C/m²).

8.1.2.2 Polytype interfaces in InAs nanopillars

The InAs nanopillars with nominal Sb concentration of 10% were grown on nanopatterned substrates by metal-organic chemical vapor deposition in the catalyst-free growth mode. HREM imaging and off-axis electron holography were carried out using a Philips CM200-FEG TEM. The sample was imaged in the diffraction mode with the diffraction lens turned off to achieve a larger field of view. The biprism voltage was set at 30 V, and the magnification was set at ~ 120 kX. The probe-corrected HAADF imaging was performed using a JEOL ARM200F TEM (camera length: 6 cm, convergence angle: 20 mrad, collection angle: 90–170 mrad). Both microscopes were operated at an accelerating voltage of 200 KV.

Figure 8.7(a) is a TEM image showing an InAs nanopillar. The box region in Figure 8.7(a), which is projected along the $[-110]$ zone axis, is shown at higher magnification in Figure 8.7(b), and the layer stacking is visible along the $\langle 111 \rangle$ direction. The region with greater stacking disorder is labeled here as the “polytype” region. Conversely, the region labeled as ZB does not show any structural change along the stacking direction. The interfaces are indicated here by dashed lines.

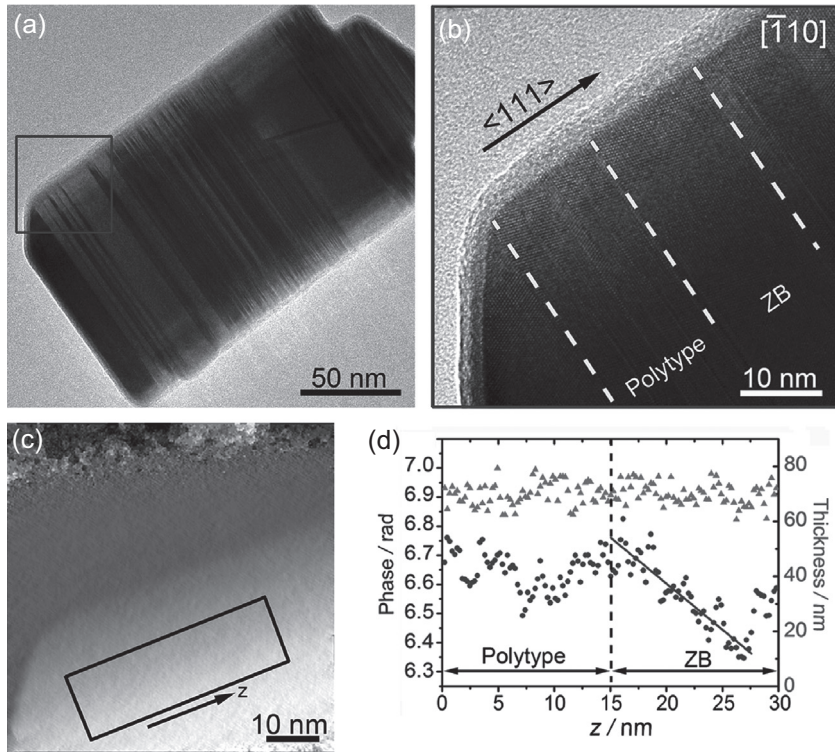


Figure 8.7 (a) TEM image of InAs nanopillar. The parallel dark lines indicate the existence of stacking disorder along the $\langle 111 \rangle$ growth direction. (b) HREM image of the box region labeled in (a) projected along the $[-110]$ direction. (c) Corresponding reconstructed phase shift image. The area for phase shift and thickness line profiles is indicated by the black box. (d) The thickness profile (triangles) is flat across the entire region; the phase shifts (disks), on the other hand, are higher with fluctuations in the polytype region, and decreasing linearly in the ZB region with a linear fit overlapped.

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The same region of the nanopillar shown in Figure 8.7(b) was then characterized using off-axis electron holography. The reconstructed phase image of a typical hologram is shown in Figure 8.7(c). The region outlined in the black box was used for phase-shift profiling, and the results are shown in Figure 8.7(d). The thickness profile of the same region is flat across the entire region, while the phase shifts are higher in the polytype region relative to the ZB region, which could be due to electrons and holes being distributed differently in the separate regions since there is no obvious indication of diffraction contrast in the image.

Closer investigation reveals that the phase shifts are linearly decreasing in the ZB region and fluctuating within the polytype region, which could be considered as equivalent to multiple WZ quantum wells embedded in a ZB matrix. While the type-II band

alignment between WZ and ZB polytype structures might lead to selective confinement of electrons to ZB-rich regions and holes to WZ-rich regions (for bulk InAs, the conduction band offset at the WZ/ZB interface is $\Delta E_c = 86$ meV, the corresponding valence band offset is $\Delta E_v = 46$ meV (Murayama & Nakayama, 1994)), SP in the WZ region could result in saw-tooth-like potentials across the WZ/ZB polytype superlattices, which are linearly increasing in the WZ region and decreasing in the ZB region (Li et al., 2012; Posternak et al., 1990). Thus, the phase-shift profile obtained here is likely to be the collective result of band offsets and SP.

The thicknesses can be obtained from the corresponding reconstructed amplitude image assuming an inelastic MFP of 57 nm for InAs. The MFP for InAs is calculated through linear extrapolation of the experimental values for AlAs (77 nm) and GaAs (67 nm) since the MFP values should be linearly proportional to the average atomic numbers (Chung et al., 2007). Only V_{sp} would contribute to the electrostatic field as compared to V_{MIP} . Thus, E_{ZB} can be calculated based on a linear fit of the experimental phase shift data in the ZB region, as shown in Figure 8.7(d): $E_{ZB} = 0.0626$ V/nm.

As mentioned before, the SP of the WZ structure could be obtained using Eqn (8.1). For our specific case, only the electric field in the ZB region is obtainable since the existing WZ regions are not wide enough to allow reliable measurements of the corresponding electric field. However, the nonzero SP in the WZ regions would lead to opposite polarization charges with equal charge density at the opposite {0001} faces of the WZ/ZB polytype superlattices, and the resulting E_{WZ} should be close to $-E_{ZB}$ to ensure supercell periodicity (Li et al., 2012; Posternak et al., 1990). Assuming $E_{WZ} = -E_{ZB}$, and taking $\epsilon_r = 15$ for InAs (Sze & Ng, 2007), the absolute value of SP present in the WZ region is calculated to be $p_{sp} = 0.0166 \pm 0.0021$ C/m².

Pure ZB InAs NWs and WZ NWs with small ZB segments are reported to have significantly distinct subthreshold characteristics, which are attributed to SP charges at the WZ/ZB interfaces, with a polarization charge density of $\geq 10^{13}$ /cm² (Dayeh, Susac, Kavanagh, Yu, & Wang, 2009). The polarization charge density σ can be converted to spontaneous polarization p_{sp} using: $p_{sp} = -\sigma$. Thus, the SP for WZ-InAs should be ≥ 0.0160 C/m², which is close to the current holography value as well as comparable to other hexagonal materials (Bernadini et al., 1997).

The spontaneous polarization is related to structures without any inversion center, and dipoles are formed by displacements of charged ions inside the crystal unit cell. The characterization of SP in ferroelectric thin films was reported using the negative spherical-aberration (Cs) imaging technique in an aberration-corrected TEM (Jia et al., 2008). Similar studies on ferroelectric heterointerfaces and nanocrystals (Nelson et al., 2011; Polking et al., 2011), as well as transition-metal oxide interfaces (Borisevich et al., 2012; Cantoni et al., 2012; Kim et al., 2012), have been carried out by STEM using probe-corrected HAADF imaging.

The aberration-corrected HREM with negative Cs is sensitive to elements of low atomic numbers (like oxygen atoms), whereas probe-corrected STEM HAADF imaging requires no postprocessing and is applicable to comparatively thick specimens. In our sample, all of the elements are easily visible in HAADF; the WZ/ZB

heterocrystalline superlattices exist only in InAs nanostructures as opposed to bulk crystals, and the corresponding projected thicknesses are normally of several tens of nanometers (the thickness of the region studied by electron holography is ~ 70 nm), which are too thick for atomic resolution with HREM. Thus, probe-corrected STEM HAADF imaging is the better choice here.

Figure 8.8(a) is a probe-corrected STEM HAADF image of a region including ZB structures as well as stacking disorder along the $\langle 111 \rangle$ growth direction within the same nanopillar used for electron holography characterization. The shear distortions in the image induced by imperfections in the STEM scanning system and the CCD camera are removed according to the ZB structure in $[-110]$ projection, and the high frequency noise is filtered using the annular mask tool in digital micrograph. For each pair of atomic dumbbells visible in this image, the bright spot should correspond to In^{3+} ($Z_{\text{In}} = 49$) and the dark spot to As^{3-} ($Z_{\text{As}} = 33$). It is clear that the dumbbell polarity is maintained across the polytype interfaces.

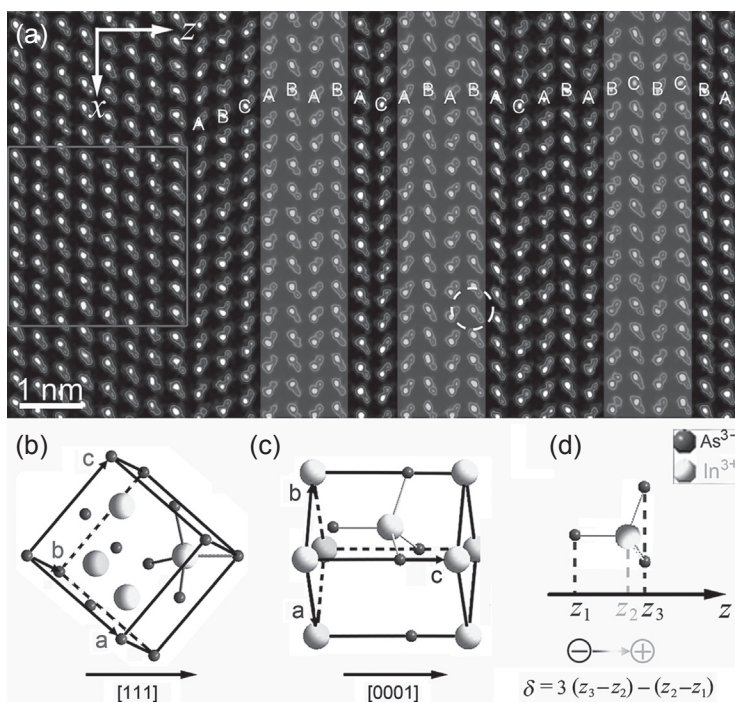


Figure 8.8 (a) Probe-corrected HAADF image of the same InAs nanopillar characterized by electron holography, including multiple stacking disorders. Three regions of WZ structure are highlighted. The white dashed circle indicates individual tetrahedral within WZ structure.

(b) and (c) are sketches of ZB and WZ unit cells with $[111]_{\text{ZB}}/[0001]_{\text{WZ}}$. (d) Model of individual tetrahedral; the displacement of charged ions within the tetrahedral could be calculated based on the projected atomic positions along z-axis.

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Three regions with local stacking sequences following the WZ structure are highlighted, as indicated in Figure 8.8(a). The unit cells for ZB and WZ structures are sketched in Figure 8.8(b) and (c), respectively. One of the WZ tetrahedral projected along the $[-2110]$ direction is shown in Figure 8.8(d), which corresponds to the region within the dashed circle in Figure 8.8a. The displacement δ between columns of In^{3+} and As^{3-} could be calculated as a difference vector between each In^{3+} and the center of mass of its four nearest neighbors of As^{3-} using: $\delta = 3(z_3 - z_2) - (z_2 - z_1)$, where the z -axis is defined in Figure 8.8(d) as pointing to the right.

Historically, probe instability has been a problem for the STEM technique. Thus, the most common imaging defects found in HAADF images including scan noise, specimen drift, and probe wobbling were corrected here using the Jitterbug software to guarantee accurate determination of the atomic positions (Jones & Nellist, 2013). However, it was found that the resulting STEM HAADF images were almost unchanged from the originals, which indicates that it was initially of high stability. A least-square fit to each of the atomic-column positions using two-dimensional Gaussian profiles is then carried out using MacTempas software, and the locations are obtained as coordinates: (x, z) . Since the z coordinate is the only parameter related to the displacement of charged ions along the c -axis, the contrast maxima positions parallel to the heterocrystalline interfaces are averaged over the vertical width of the figure to lower the level of random noise.

The pure ZB region framed within the box in Figure 8.8(a) is treated with the crystallographic image processing tool in MacTempas software, with which the displacements of atoms from their ideal positions in the image due to random noise can be averaged. Figure 8.9(a) shows the resulting processed image. The atoms are found to be perfectly aligned in the vertical direction. The value of displacement δ within the tetrahedral is calculated over the whole image, which appears periodically to be 0 or 1 pixel (1 pixel = 0.0148 nm). Considering the residual random noise and the limitations imposed by the finite pixel size, tetrahedral with ZB structure should be centrosymmetric without any SP.

The displacement δ is calculated for all of the highlighted WZ regions in Figure 8.8(a). The result shows that the tetrahedral bond along the c -axis is always longer than the other off-axis bonds, resulting in a dipole moment pointing to the right, as shown in Figure 8.8(d). Thus, there should be positive polarization charges accumulated at the WZ/ZB interface and negative polarization charges at the ZB/WZ interface, which would result in linearly decreasing phase shifts across the ZB region, as was the case measured by electron holography in the current study.

The empirical rule of Chelikowsky and Philips states that those WZ structures that are unstable compared to the corresponding ZB structures should have c/a ratios greater than ideal, while this ratio should be less than ideal for stable WZ structures (Chelikowsky & Philips, 1978). While the WZ structure is comparatively unstable for InAs (Yeh, Lu, Froyen, & Zunger, 1992), the corresponding c/a ratio for WZ structure is expected to be slightly larger than that calculated geometrically from the cubic bulk lattice constant.

The lattice parameters of ZB-InAs and WZ-InAs are carefully measured in Figure 8.8(a) with the atomic positions obtained from the peak-finding algorithm.

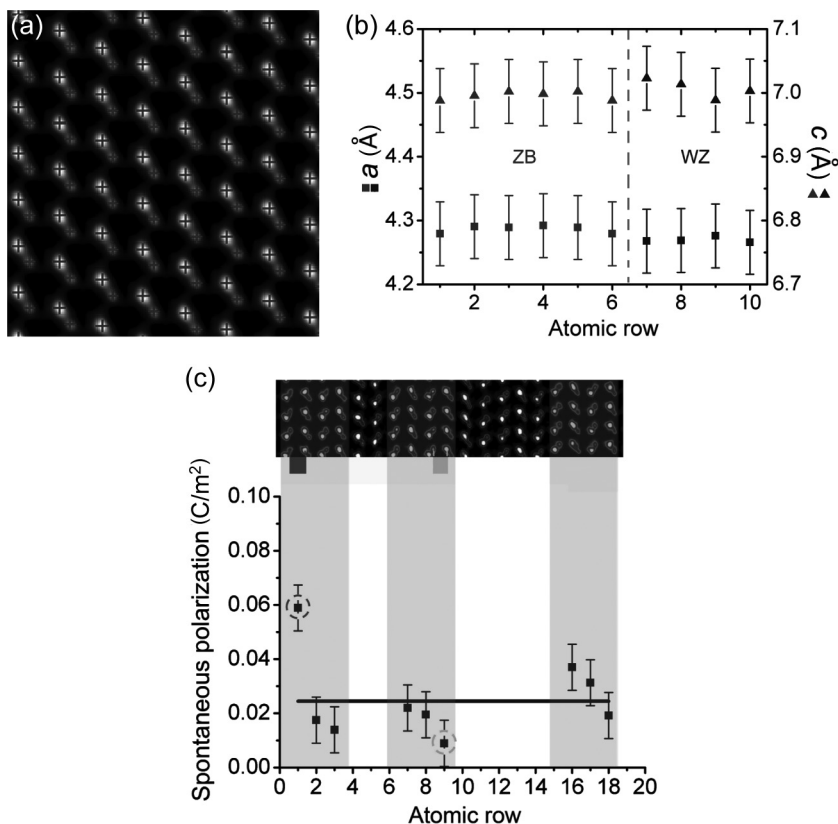


Figure 8.9 (a) Probe-corrected HAADF image of the box region in Figure 8.8(a), treated by the crystallographic image processing tool in MacTempas software. The crosses are overlapped to indicate the exact atomic positions. (b) Measurements of lattice parameters perpendicular (triangles) and parallel (squares) to the ZB/WZ interface. The error bar of ~ 0.1 Å is determined considering the finite pixel size of the experimental HAADF image and the accuracy of the peak-finding algorithm. (c) The squares represent measured values of local spontaneous polarization in the highlighted WZ regions, with the largest and smallest values labeled by dashed circles. The horizontal widths of the squares at the top indicate the largest and the smallest tetrahedral bonds along c -axis, respectively. The horizontal line is spontaneous polarization averaged over all of the individual data points. The error bar of ~ 0.0085 C/m^2 is obtained through error propagation of errors in measurements of atomic displacements and the lattice parameter of WZ structure.

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The average value of the lattice parameter a_{ZB} obtained from ZB-InAs is calibrated according to the generally accepted cubic bulk lattice constant for InAs ($a_{\text{ZB}} = 6.058$ Å) (Madelung, 2004) to correct for the slight magnification deviation of the microscope. The measurements are carried out perpendicular to the ZB/WZ interface as well as parallel to the interface, and the results are presented in Figure 8.9(b).

The lattice parameters of WZ structures obtained only through geometric conversion from their corresponding ZB structures are related to a_{ZB} and hexagonality of different polytypes p by [Kriegner et al. \(2011\)](#):

$$a_{\text{geom}, p} = a_{\text{ZB}}/\sqrt{2} \quad \text{and} \quad c_{\text{geom}, p} = a_{\text{ZB}}p/\sqrt{3} \quad (8.2)$$

where p is 2 for WZ structure. In this way, the lattice parameter for ZB structure is geometrically converted to equivalent WZ structures for direct comparison. The average values of the measured lattice parameters for WZ structures are $a_{\text{WZ}} = 4.269 \text{ \AA}$, $c_{\text{WZ}} = 7.005 \text{ \AA}$; and the average values obtained from geometric conversion of ZB parameters are $a_{\text{geom}, p} = 4.284 \text{ \AA}$, $c_{\text{geom}, p} = 6.996 \text{ \AA}$. Thus, the actual WZ unit cell is indeed slightly stretched along the c -axis and contracted in the plane perpendicular to the c -axis.

The SP can be calculated utilizing the experimental lattice parameters of WZ structure, the atomic displacement δ , and the Born effective charge values of the ions. The effective charges for In^{3+} and As^{3-} in the WZ structure are calculated using the Berry phase expression based on first-principles calculations implemented in VASP, which are 2.80 for In^{3+} and -2.60 for As^{3-} along the c -axis. The calculated SP values for the three WZ regions are shown in [Figure 8.9\(c\)](#). The averaged value is $p_{\text{sp}} = 0.0245 \text{ C/m}^2$, which is of the same order of magnitude as the value obtained from the electron holography analysis, as well as from estimates based on published measurements.

Moreover, the obtained p_{sp} values are nowhere near constant across the WZ regions with the largest value of 0.0589 C/m^2 and the smallest value of 0.0089 C/m^2 . The variations of p_{sp} across the WZ regions are reasonable, for reasons stated below. Polytypes with different stacking sequences have slightly different lattice parameters, and the corresponding distortions from the ZB counterparts are reported to increase linearly with hexagonality ([Kriegner et al., 2011](#)).

In our case, the WZ regions are sandwiched between other polytypes, and the lattice mismatch at the interfaces would introduce strain, which would penetrate through the WZ regions of only two unit cells in width and further distort the tetrahedral bonds. Thus, it seems that the individual p_{sp} value is more meaningful than the average value since it reflects the local displacements within the tetrahedra at atomic resolution and their variation along the interface normal, which verifies the significance of probe-corrected HAADF imaging for characterizing the SP across the polytype heterocrystalline interfaces.

8.1.3 In situ observation of charges and electrostatic fields within nanowires

Electron holography is an electron interferometry technique, which can provide amplitude and phase information simultaneously. The latter has been used to characterize the magnetostatic and electrostatic fields in and around samples. With *in situ* bias inside a TEM, the electron holography technique can also find applications in studying the

threshold for electron field emission of carbon nanotubes (Cumings et al., 2002) and the electrical contacts at the semiconductor NW tips (Gan et al., 2013; He et al., 2013).

8.1.3.1 Field-emitting carbon nanotubes

A carbon nanotube is independently voltage biased, and the electron fields emitted from the nanotube are transferred predominantly horizontally and collected by a gold collector plate. A specially constructed piezo-driven manipulation stage (Wang, Poncharal, & Heer, 2000) was used inside a Phillips CM200 FEG microscope utilizing a Lorentz lens. Multiwall carbon nanotubes grown by the conventional arc-plasma method (Ebbesen & Ajayan, 1992) were mounted to the manipulation electrode using conductive epoxy and positioned about 6 μm away from the gold electrode, and a biased voltage, V_b , was applied between the two. Field emission current was monitored using a DL Instruments 1211.

Figure 8.10 shows in the left-hand column a series of phase-shift maps reconstructed from holograms recorded at selected nanotube bias V_b , both below and above the threshold for nanotube electron field emission. The upper phase-shift map is for $V_b = 0$ V, and the featureless area around the nanotube indicates a uniform phase. The nanotube itself appears, from which a mean “inside” potential for the nanotube of 12 V is obtained. This value is in agreement with previous measurements on other carbon materials (Lin & Dravid, 1996).

The center and lower phase shift maps in the left-hand column of Figure 8.10 are calculated from electron holograms taken at $V_b = 70$ V and $V_b = 120$ V, just above and significantly above the threshold bias for field emission for this nanotube. In these modulo- 2π plots, wherever the phase shifts by 2π it wraps back to zero, causing stripes in the phase maps, which are strikingly different from the unbiased case. These stripes show the equiphase contour lines of the original hologram.

The right-hand column of images in Figure 8.10 represents phase gradient data, which are determined by calculating the magnitude of the two-dimensional gradient directly from the phase shift maps shown to the left. For $V_b = 0$ V, the phase gradient is featureless around the nanotube. On the other hand, the phase gradient is clearly concentrated at the tip of the nanotube for $V_b = 70$ V and $V_b = 120$ V.

The phase shift maps in the left-hand column of Figure 8.10 qualitatively represent electric potential maps, and the equiphase lines are fair representations of the equipotential lines in the region around the nanotube. Additionally, the phase gradient maps of Figure 8.10 are fair qualitative representations of the electric field strength external to the nanotube. Most importantly, the high phase gradient at the tip of the biased nanotube demonstrates that the electric field is most intense at the tip of the nanotube, and sidewall defects or other field concentrating geometric or electronic irregularities are not required for field emission.

8.1.3.2 Si nanowires with p–n junctions: unbiased and biased

The Si NWs with axial p–n junctions studied here were grown in a cold-wall chemical vapor deposition reactor via the VLS method using 30–60 nm diameter Au colloid

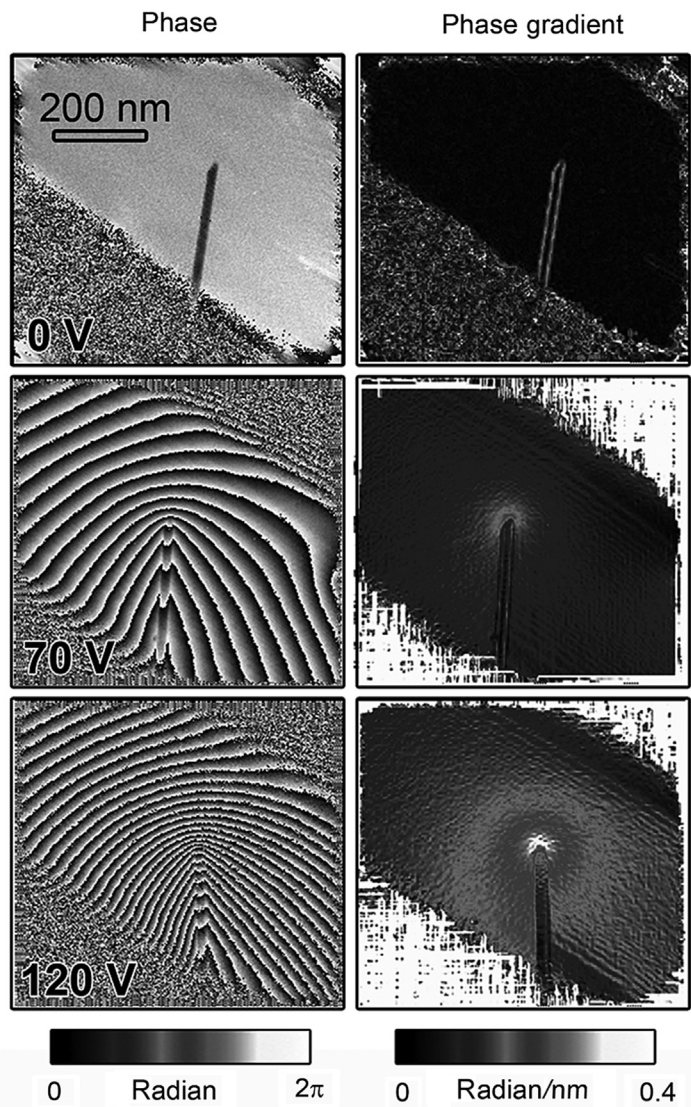


Figure 8.10 Phase shift and phase gradient maps extracted from holograms of the same carbon nanotube at bias voltage $V_b = 0, 70, 120$ V. The phase gradient indicates where the electric field is the strongest. While $V_b = 0$ V shows no sign of electric field at the tip of the nanotube, 120 V shows the strongest tip electric field.

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nanoparticle catalysts on silicon (111) substrates. A $\sim 10\text{-}\mu\text{m}$ -long phosphorus-doped (n-type) Si segment was initially grown using the gas mixture of SiH_4 and PH_3 at a growth temperature of 550°C and total pressure of 3 Torr with an estimated doping concentration of $\sim 10^{19}/\text{cm}^3$. The PH_3 gas was then turned off, and a $\sim 300\text{ nm}$ segment of pure unintentionally doped Si was grown before termination of growth. The corresponding dopant concentration was estimated to be roughly 10^{17} to $10^{18}/\text{cm}^3$ (Ingole, Manandhar, Chikkannanavar, Akhadov, & Picraux, 2008). Electron holography was carried out using Phillips CM200 FEG microscope at Lorentz mode.

According to the corresponding TEM image of the Si NW, the change of doping during NW growth did not appear to introduce any kinking or defects. Some small Au particles were present on the NW surface due to surface diffusion of Au from the catalyst particle during growth (Allen et al., 2008). However, these particles were limited to a region of $\sim 80\text{ nm}$ from the NW tip, and their amount was small with a concentration of $\sim 10^{11}/\text{cm}^2$, so that they were not expected to have a significant effect on the measurements of electrostatic potential profile across the p–n junction.

Figure 8.11(a) and (b) are electron hologram of the Si NW and corresponding reconstructed phase image, respectively. The phase profile in Figure 8.11(c), taken along the arrow pointing down from the Au tip, shows a monotonic decrease in phase to zero moving away from the tip, which indicates that the catalyst is positively charged, most likely due to secondary electron emission under the high-energy electron beam used during imaging. The phase profile across the NW shown in Figure 8.11(d) suggests that the NW cross-section is approximately round. The flat phase in the surrounding vacuum region suggests that the NW surface charge is small.

The phase shift profile along the length of the NW is shown in Figure 8.11(e). In order to remove the phase shift due to the projection of the electric field in vacuum caused by charging at the Au catalyst tip, a similar line profile is extracted from the vacuum region along the edge of the NW and then subtracted from the NW phase profile. The difference is the phase profile due only to the NW, as shown in the subtracted phase of Figure 8.11(e). It appears that the phase near the tip is largely affected by the charging at the Au particle, whereas the phase around the p–n junction remains unchanged because the fringing electrostatic field from the Au particle has been attenuated there.

Based on the subtracted phase, an average built-in potential profile was calculated and presented in Figure 8.11(f). A Gaussian filter is then applied to the profile to remove high frequency noise. The potential step located at $\sim 300\text{ nm}$ coincides with the position of the p–n junction, while the potential drop located near $\sim 100\text{ nm}$ possibly indicates the formation of a Schottky contact between the Au catalyst and the Si NW (He et al., 2013). The p–n junction height is estimated to be $1.0 \pm 0.3\text{ V}$. In contrast, the Schottky contact has a barrier height of $0.5 \pm 0.3\text{ V}$. We note that the apparent drop in potential visible at $\sim 25\text{ nm}$ from the Au catalyst is likely to be due to a Fresnel fringe from the Au particle.

In order to better interpret the electrostatic potential profiles, simulations of the NW potential distribution were performed using the Silvaco™ software package. The size

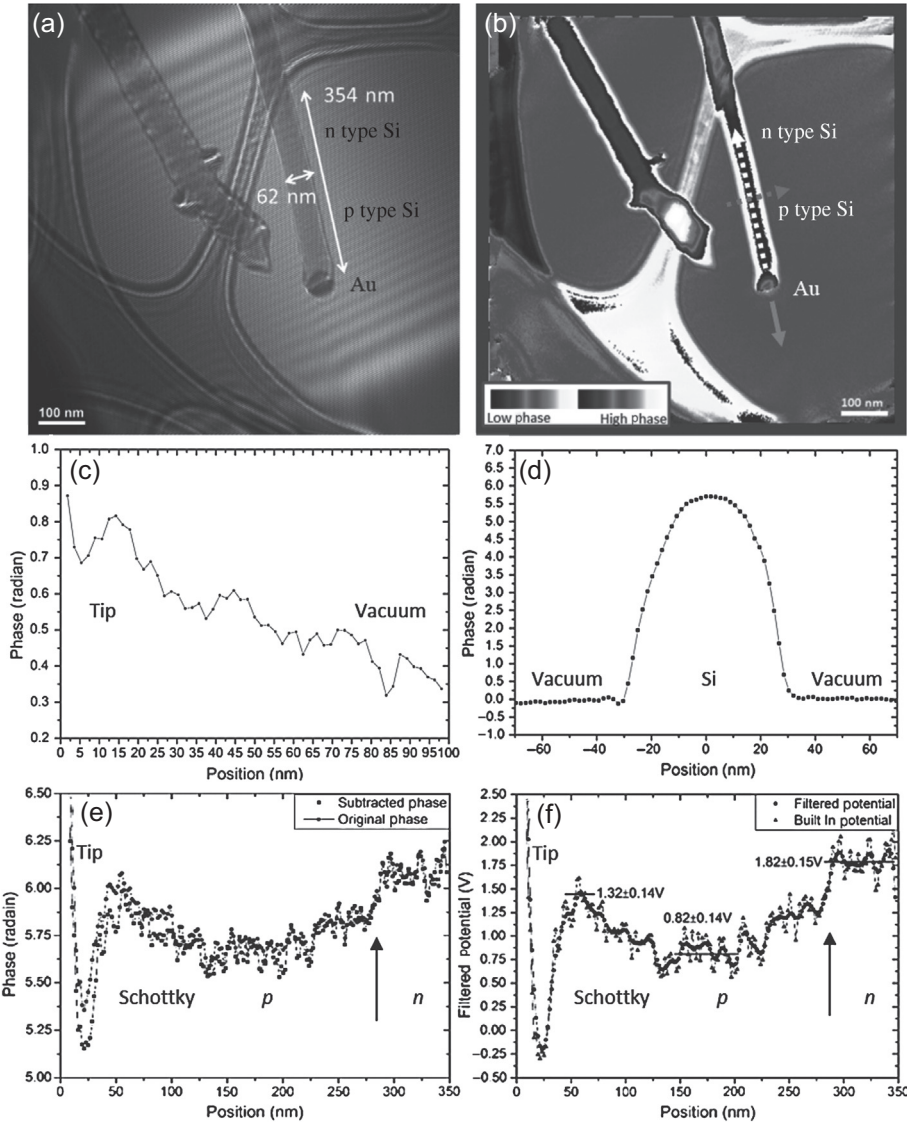


Figure 8.11 (a) Hologram of Si NW including p–n junction supported on holey carbon film. (b) Reconstructed phase image with pseudo-color. (c) Phase shift line profile along the gray arrow pointing down in (b). (d) Phase shift profile across the Si NW along the dotted gray arrow pointing to the right in (b). (e) The original and vacuum subtracted phase shift line profile along the dotted white arrow point up in (b). (f) Built-in potential along the Si NW before and after Gaussian filter.

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parameters for the simulation are schematically illustrated in Figure 8.12(a), which are obtained from experimental data. Since the effect of the surface charge was not apparent in the experimental results, the surface charge in the simulation was estimated to be zero at the interface between Si and SiO₂. The validity of this assumption was tested in additional simulations with varying surface charges, as discussed below.

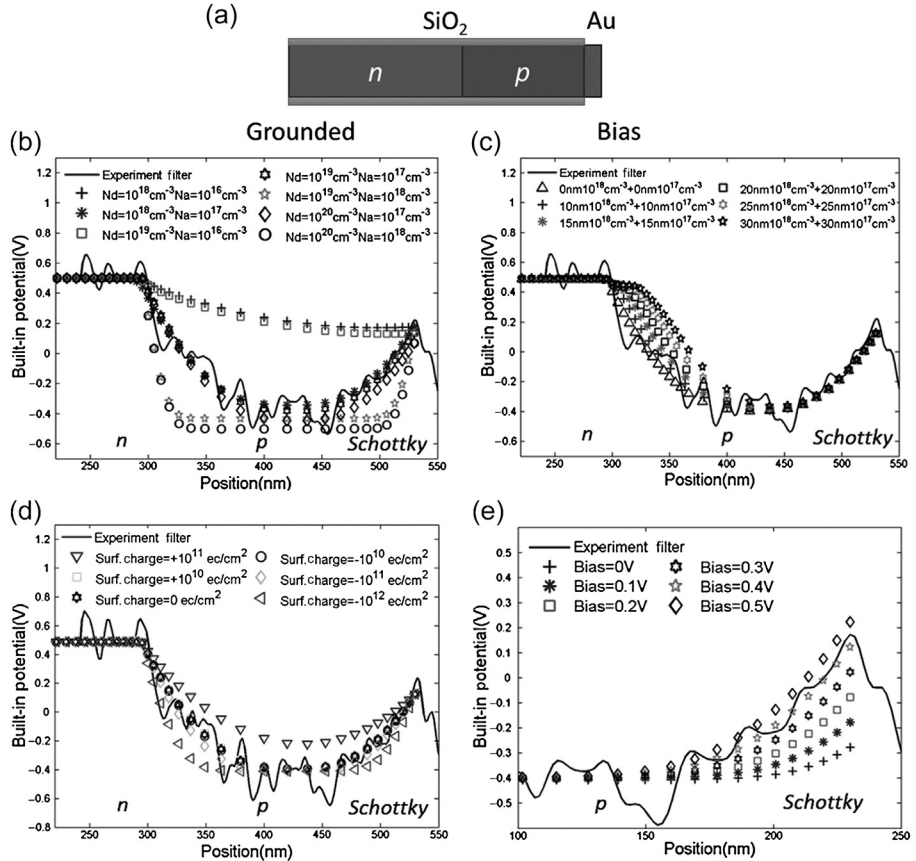


Figure 8.12 (a) Schematic of the cross-sectional model for the Si NW with p–n junction, which is grounded on the n -side and biased on the Au particle at the end of the p side. (b) Experimental and simulated built-in potentials for different dopant concentrations at the p–n junction, work function $\phi = 4.6 \text{ V}$ is used. (c) Experimental and simulated built-in potentials with different gradient widths. The dopant concentrations $N_A = 10^{17}/\text{cm}^3$, $N_D = 10^{19}/\text{cm}^3$ and $\phi = 4.6 \text{ V}$ are used, which gives the best fit to experiment in (a). Two layers in the dopant concentrations of $N_D = 10^{18}/\text{cm}^3$ and $N_D = 10^{17}/\text{cm}^3$ are added with different layer widths. (d) Experimental and simulated built-in potentials with different surface charges ($N_A = 10^{17}/\text{cm}^3$, $N_D = 10^{19}/\text{cm}^3$ and $\phi = 4.6 \text{ V}$). (e) Experimental and simulated built-in potentials with different bias on a single Schottky diode ($N_A = 10^{17}/\text{cm}^3$, and $\phi = 5.0 \text{ V}$).

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The n-type segment of the Si NW was connected to ground, while the p-type segment was connected to Au catalyst particle via a Schottky contact with bias applied to the Au tip. The donor and acceptor concentrations, Au work function, and bias were then systematically adjusted to find a match with the experimental electrostatic profile.

As shown in Figure 8.12(b), a donor concentration of $\sim 10^{19}/\text{cm}^3$, an acceptor concentration of $\sim 10^{17}/\text{cm}^3$, a work function of 4.6 V and 0 V bias gave the best fit to the experimental profile. The corresponding simulated built-in potential height and depletion length for the p–n junction were 0.93 V and 120 nm, respectively, and 0.51 V and 100 nm for the Schottky contact, respectively. These simulated values are consistent with the experimental values.

Any change in dopant concentration during VLS growth usually results in an exponentially decreasing gradient at the interface (Perea, Li, Dickerson, Misra, & Picraux, 2011) with a length that is comparable to the NW diameter, which is ~ 60 nm in the current case. To assess the effect of such gradients, two n-type segments with concentrations of $10^{18}/\text{cm}^3$ and $10^{17}/\text{cm}^3$, respectively, were added to the junction region, as shown in Figure 8.12(c). The simulations suggest that the short n[−] portion is fully depleted and has only a small effect on the p–n junction, making the junction slightly flatter in the middle. While the total depletion length is very long compared to the gradient due to low concentration on the *p* side, the gradients do not have a significant effect on the junction height or the total depletion width.

A conformal native oxide is usually observed on Si NW surface resulting in interface charge or surface states around the NWs (Hertog et al., 2009; Ingole et al., 2008). However, the flat phase observed in vacuum near the NW indicated that the possible interface charge was too small to be directly detected by phase change in the present measurements. To investigate possible effects of the interface charge on the inferred dopant profiles, various surface charges were assumed in the simulations. It was found that a charge density of 10^{11} electron/ cm^2 did not have significant effect on the results, as shown in Figure 8.12(d).

A closer look at the phase image at the edge of the NW shows that the edge is of equal phase across the p–n junction, which suggests that the potential is pinned at mid-gap at the NW surface, which could indicate a small depletion region at the NW surface due to surface states (Cooper et al., 2010). The possible existence of the depletion region may also cause somewhat lower measured dopant concentrations since averaged values are being measured through the thickness.

Si NWs with Au contacts have been reported to form Schottky barriers due to their differences in Fermi level (He et al., 2013; Koren et al., 2011), which is consistent with our observations. If only active dopants and bias applied to the barrier are considered, the built-in potential can be expressed as

$$V_{\text{bi}} = \chi + \frac{E_{\text{c}} - E_{\text{f}}}{q} - \phi + V_{\text{bias}} \quad (8.3)$$

where χ is the electron affinity for silicon, E_{c} is the conduction band energy, E_{f} is the Fermi level, q is the electron charge, ϕ is the Au work function, and V_{bias} is the bias applied to Au (Sze & Ng, 2007). Simulation applying different bias voltages

(Figure 8.12(e)) reveals that a biased Schottky diode with 0.4 V bias without p–n junction shows a very good fit with the experimental profile.

Since the Au is positively charged, the Schottky contact should be in reverse bias. The Fermi level on the Au side will be lower, increasing the height of the Schottky built-in potential. If the Si *p* side remains grounded and its Fermi level stays flat, the bias will only change the Fermi level across the Schottky contact, which is equivalent to applying bias to a single Schottky diode without p–n junction. Simulations with a lower work function of 4.6 V than the value reported in the literature of ~ 5 V (Yao & Wang, 2005) give the best fit here. Therefore, such bias can be considered as a change of work function in the simulation that keeps the Fermi level flat across the p–n junction.

In a similar electron holography study of doped p–n junctions in Si NWs and related biased Schottky barriers (He et al., 2013), a built-in potential of 1.03 ± 0.17 V and a depletion width of ~ 286 nm are obtained applying off-axis electron holography technique, for ~ 10 - μm -long n-type segment, ~ 3 - μm -long p-type segment. The diameter of the Si NW under study is ~ 120 nm. Similar electron holography observations were carried out when a positive or negative voltage was applied to the Si NW. However, no obvious difference of phase change was detected at the p–n junction region relative to the unbiased condition.

The *in situ* electrical transport measurements were performed on an individual Si NW when the Au tip of the NW is in point contact with the Pt probe, and the result of the corresponding current–voltage (*I*–*V*) measurement is shown in Figure 8.13. It is noted that this *I*–*V* curve displays an inverted rectification behavior for the expected p–n junction configuration, which agrees with a hypothesized Schottky contact between the Pt probe tip and the p-type Si NW with very high resistivity. Thus, during the *in situ* biasing experiment, the actual voltage applied on the Si p–n junction

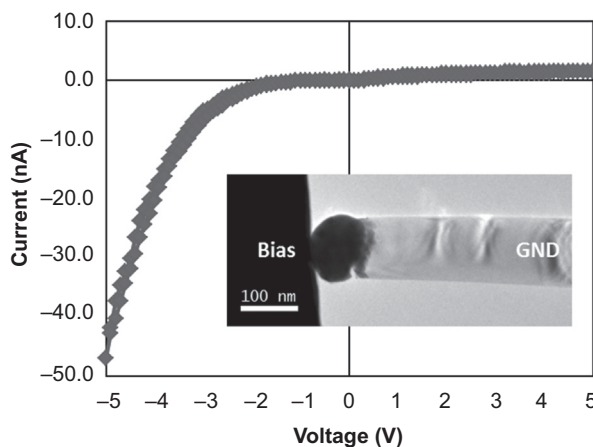


Figure 8.13 *I*–*V* curve measured through *in situ* end-contacted Si NW, where the Au tip of the NW is in point contact with the Pt probe. Corresponding inset shows the device geometry. Reprinted with permission from He et al. (2013). Copyright (2013) IOPscience.

itself is too low to create an appreciable shift of the energy bands, and the hologram in this region shows no detectable influence of the bias.

On the other hand, the bias shows a strong influence on the electron holograms obtained in the vicinity of the Si NW tip. Figure 8.14 shows line profiles of the phase shift along the Si NW at bias of ± 3 V. The data points in the dotted line around $\sim 1.7 \mu\text{m}$ away from the Au tip are artifacts due to the strong electron diffraction caused by local bending of the NW. However, it does not affect the overall trend of the phase shifts.

When -3 V is applied to the NW tip, the Schottky barrier is forward biased, with R_c only a few times greater than R_{NW} . Thus, the potential has a modest jump at the Schottky contact, followed by a linear increase with comparatively smaller slope toward the NW base. On the other hand, when $+3$ V is applied, the Schottky barrier is reverse biased, with $R_c \gg R_{NW}$. Thus, almost all the potential drop is in the contact region, leaving the NW near ground potential. The occurrence of Schottky barrier has been commonly found in numerous Si NWs, which may possibly be attributed to lower effective doping levels near the tip due to the presence of compensating surface states (Ingole et al., 2008), and perhaps a surface work-function difference caused by surface oxidation and/or defects (Giordano, Cinquini, & Pacchioni, 2006; Ishikawa et al., 1997).

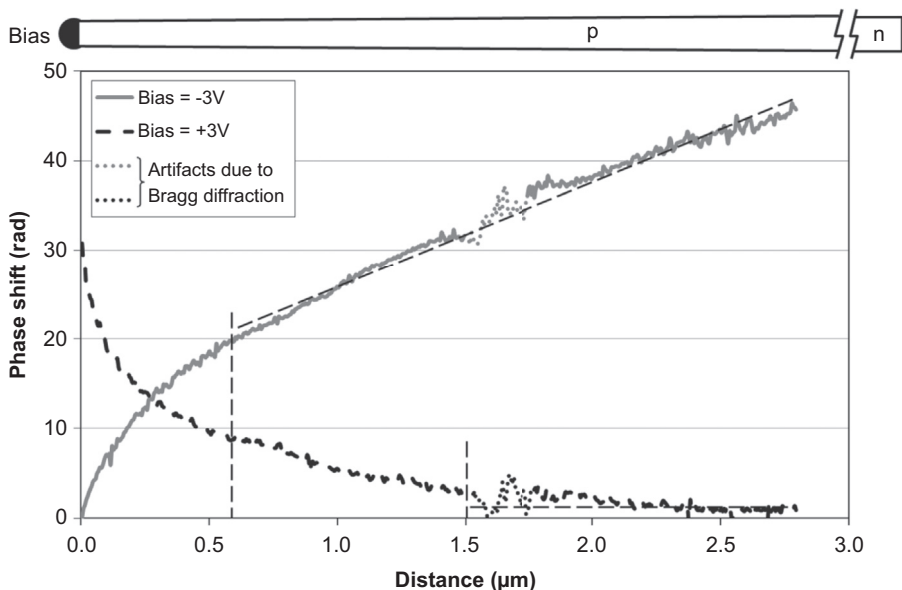


Figure 8.14 Phase profiles along the Si NW from the Au tip toward the substrate under applied bias of -3 V and 3 V to the NW tip. Dotted lines indicate artifacts due to strong diffraction contrast at the local area. Dashed lines are eye guiding, indicating the trends of the phase shift profile and the approximate depletion width of the Schottky barrier.

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8.2 Sources of future information and advice

The pink book ‘*Introduction to electron holography*’ (Kluwer Academic/Plenum Publisher, New York) would be a great book to start with, which discusses all aspects of electron holography by experts in this area. The reviews by Geiger, Lichte, Linck, and Lehmann (2008); Lichte et al. (2007); Lichte & Lehmann, 2008; McCartney and Smith (2007) provide up-to-date information about where electron holography is currently focused. Nowadays, there are plenty of research groups working on characterization of materials using electron holography, that is, Prof. Martha McCartney from Arizona State University where I obtained my doctoral degree; Prof. Hannes Lichte from Technische Universitaet; Prof. Rafal Dunin-Borkowski from Ernest Ruska-Center for Microscopy and Spectroscopy with Electrons, Jülich; Prof. Yimei Zhu from Brookhaven National Laboratory; Prof. Martin Hÿtch from CEMES-CNRS; Dr. Martien I. den Hertog from INAC/SP2M/LEMMA; and myself (Luying Li) from Huazhong University of Science and Technology, to name a few.

Acknowledgements

Thanks to Prof. Martha McCartney and Prof. David Smith for their great support to all of my research work presented in this chapter. Thanks also to the National Natural Science Foundation of China (51371085, 11304106), MOE Doctoral Fund (20120142120059), and the Fundamental Research Funds for the Central Universities (HUST: 2012QN107), SRF for ROCS, SEM, DOE Grant DE-FG02-04ER46168 (ASU) for financial support. The author also gratefully acknowledges the use of facilities at the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.

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Electron holography of nanowires — Part 2

9

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9.1 Introduction to electron holography

In this chapter a specific transmission electron microscopy (TEM) technique, called off-axis electron holography, is described. As for any TEM technique the sample needs to be sufficiently thin to allow electrons to traverse the specimen. First I will introduce the technique, and describe the basic concepts and the type of signals that can be measured by holography. A comparison between 2D samples and nanowires (NWs) is presented to show challenges and solutions for both types of samples and the necessary sample preparation. After a review of literature on holography of NWs and particles, I will show results where holography was used to study dopant characterization in modulation-doped silicon NWs, and characterization of electric fields in GaN—AlN NW heterostructures. More examples of applications of electron holography on NWs will be presented in the next chapter. The idea of the present chapter is to give a flavor of what holography is and can do with a minimum of equations, and also to describe the challenges that we face to get quantitative information on NWs by electron holography. At the end of the chapter you will find a conclusion and perspectives and further suggested reading material on holography.

9.1.1 What is electron holography?

In 1947 Dennis Gabor, a Hungarian-British physicist, proposed the method of interference imaging and gave it the name holography, from a Latin word meaning “whole writing.” His idea was that using interference imaging, the phase and amplitude of the electrons could be recorded separately, and aberrations due to the electron lenses could be removed from the phase image, allowing a higher resolution (Gabor, 1948).

The principle of any holographic technique is to interfere with a wave that contains (phase and amplitude) information of the sample with a reference wave. If electrons are used as the wave, 20 forms of holography can be distinguished (Cowley, 1992), but here we will restrict the description to only one form: off-axis electron holography. Electron holography is a powerful tool since electrical and magnetic properties of the sample can be measured simultaneously (Midgley, 2001), although in the following we will focus on the electrical properties of semiconducting nanowires (NWs).

In off-axis electron holography, a part of the sample is illuminated with a broad parallel beam. The electrons that passed through the sample (with wave vector k_{obj}) interfere with the electrons that passed the vacuum (with wave vector k_{ref}) due to a

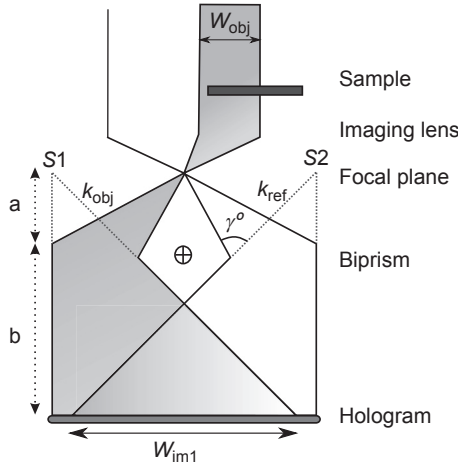


Figure 9.1 Schematic diagram that illustrates the principle of off-axis electron holography. A wire to which a potential is applied, the biprism, is used to interfere a reference wave (with wave vector k_{ref}) with the object wave (with wave vector k_{obj}). $S1$ and $S2$ are the two virtual sources that interfere, forming an interference pattern or hologram of width W_{im1} . The width of the object wave is W_{obj} . γ is the deflection angle of the wave due to the action of the biprism. Adapted from Cooper (2006).

metal-coated quartz wire to which a potential U_b is applied: the biprism. In the image plane we obtain an interference pattern of the two waves, also called the hologram, as shown schematically in Figure 9.1. An example of a hologram obtained in the vacuum is shown in Figure 9.2(a).

The wave function that passed through vacuum is called the reference wave, Ψ_{ref} , and the wave function that passed through the sample is called the object wave, Ψ_{obj} . At the level of the detector, the intensity of the two interfering image waves is measured, given by (Lichte, 2008; Midgley, 2001; Völkl et al., 1999)

$$\begin{aligned}
 I_{\text{holo}}(\vec{r}) &= \left| \Psi_{\text{ref}} + \Psi_{\text{obj}} \right|^2 \\
 &= \left| A_{\text{ref}} \exp(i2\pi k_{\text{ref}} \vec{r} + i\phi_{\text{ref}}) + A_{\text{obj}} \exp(i2\pi k_{\text{obj}} \vec{r} + i\phi_{\text{obj}}) \right|^2 \\
 &= A_{\text{ref}}^2 + A_{\text{obj}}^2(\vec{r}) + 2A_{\text{ref}}A_{\text{obj}}(\vec{r}) \cos \left[2\pi(k_{\text{obj}} - k_{\text{ref}}) \vec{r} + \Delta\phi(\vec{r}) \right]
 \end{aligned} \tag{9.1}$$

where $\Delta\phi(\vec{r}) = \phi_{\text{obj}}(\vec{r}) - \phi_{\text{ref}}$ is the difference in phase between the object and the reference wave. The amplitude information is contained in the contrast of the fringes, and is also influenced by the partial coherence of the electrons and other transmission electron microscopy (TEM) imperfections that are omitted in the equation. The phase information $\Delta\phi(\vec{r})$ is contained in modifications of the carrier frequency q_c , given by $k_{\text{obj}} - k_{\text{ref}}$, the location of the fringes (Lichte, 2008). Off-axis electron holography

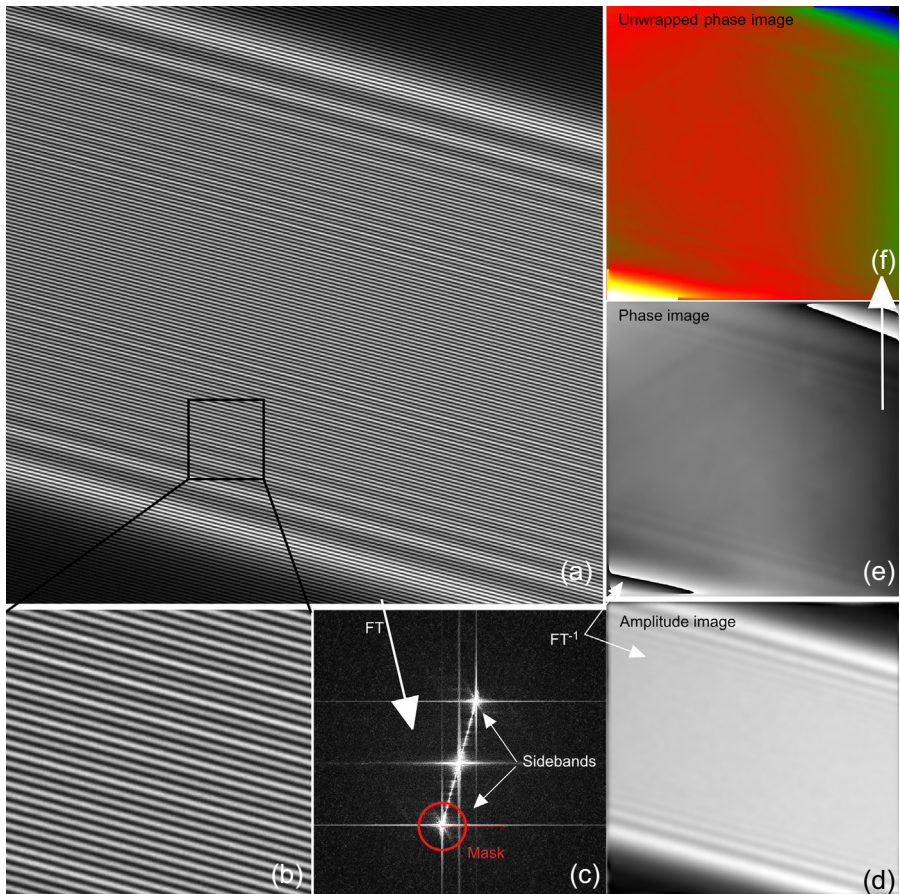


Figure 9.2 The reconstruction procedure of a hologram. (a) Hologram obtained in a vacuum. (b) Zoom of the indicated region showing the carrier frequency. (c) The Fourier transformation showing the center band (the first two terms in Eqn 9.3) and the two sidebands (the last two terms in Eqn 9.3). A mask is applied to one of the two sidebands. The inverse Fourier transformation of the filtered FT results in the complex image that is composed of (d) the amplitude and (e) the phase component. (f) The unwrapped phase image.

therefore allows direct measurement of the amplitude and phase of the image wave, something that is impossible using conventional TEM. The next step is extracting the phase and amplitude information from the hologram.

9.1.2 Hologram reconstruction procedure

We showed that the intensity in the hologram is described by a modulated cosine function (Eqn 9.1), and that the phase information is contained in the frequency of the interference fringes.

Historically hologram reconstruction was performed using a light optical reconstruction method on an optical bench. Since fast computers and digital recording using CCD cameras are available, roughly two types of reconstruction techniques can be distinguished, which either fit a function to the hologram intensity in direct space (Fujita, Yamamoto, McCartney, & Smith, 2006; Lehmann, Völkl, & Lenz, 1994) or use filtering in reciprocal space (Völkl et al., 1999).

The first method has the advantage of being faster, and could result in a higher resolution (or larger field of view at the same resolution), since it is no longer required to sample the finest detail with two to three fringes. The problem of reconstruction techniques using real space is that the intensity in the hologram is not only described by the cosine function of the carrier frequency, but contains modulations of lower spatial frequency due to Fresnel fringes caused by diffraction on the biprism, and these modulations limit the accuracy of the fit if they are not included in the model.

The second reconstruction technique makes use of a Fourier transformation (FT). Filtering in reciprocal space is performed by multiplication with a mask of the FT to select the sideband, and then the FT is inverted back to obtain the 2D map of dephasing of the wave compared to the reference wave. For convenience the reference amplitude A_{ref} is set to 1.

To reconstruct the hologram the Fourier transformation of the intensity (Eqn (9.1)) is expressed:

$$\text{FT}(I_{\text{holo}}(\vec{r})) = \text{FT}(1) + \text{FT}\left(A_{\text{obj}}^2(\vec{r})\right) + \text{FT}\left(2A_{\text{obj}}(\vec{r})\cos(2\pi\vec{q}_c\vec{r} + \Delta\phi(\vec{r}))\right) \quad (9.2)$$

Generally this is rewritten as (Völkl et al., 1999)

$$\begin{aligned} \text{FT}(I_{\text{holo}}(\vec{r})) = & \delta(\vec{q}) + \delta(\vec{q}) \otimes \text{FT}\left(A_{\text{obj}}^2(\vec{r})\right) + \text{Center band} \\ & \delta(\vec{q} - \vec{q}_c) \otimes \text{FT}\left(A_{\text{obj}}(\vec{r})\exp(i\Delta\phi(\vec{r}))\right) + \text{Sideband} - \vec{q}_c \\ & \delta(\vec{q} + \vec{q}_c) \otimes \text{FT}\left(A_{\text{obj}}(\vec{r})\exp(-i\Delta\phi(\vec{r}))\right) \text{Sideband} + \vec{q}_c \end{aligned} \quad (9.3)$$

The equation contains four terms. A Dirac peak at the origin ($\vec{q} = 0$) describes the uniform intensity of the reference wave. A second peak at the origin describes the intensity distribution in a conventional TEM image (amplitude attenuation of the wave). A peak centered at the frequency $\vec{q} = -\vec{q}_c$ contains the phase information of the image-wave function, and a peak at $\vec{q} = \vec{q}_c$ corresponds to the complex conjugate of the image-wave function. The last two peaks represent the sidebands in the reciprocal space and are also indicated in Figure 9.2, where the reconstruction procedure is illustrated schematically. These sidebands contain the phase information we would like to extract. Both sidebands contain the same phase information, only the sign of the phase will change. Obviously for the interpretation of the phase image the

sign is important, so we should be careful which sideband we use for reconstruction. A mask is positioned around one of the sidebands to remove all other frequencies and select only the frequencies present in the sideband. The size of the mask determines the spatial frequency sampling of reciprocal space, and inversely, the region of direct space where the information is averaged. A large mask favors a high spatial resolution and a small mask a good signal-to-noise ratio. It is important to realize the influence of the mask on the spatial resolution in the phase image: an atomically abrupt transition will be smeared out over a larger region, depending on the mask size, in the phase image. In [den Hertog \(2009\)](#), reconstructions with different mask sizes are shown of a simulated abrupt interface to assess the influence of the mask. A good compromise of the mask size leads to a spatial resolution of approximately three times the fringe spacing. Once the mask is applied, the sideband is moved to the origin of reciprocal space and an inverse FT is performed to obtain the phase and amplitude images.

Phase fluctuations are visible in the phase image ([Figure 9.2\(e\)](#)) that was obtained from an empty hologram. This illustrates that aberrations in the projector system and in lenses and imperfections of the CCD camera (due to shear distortion in their transfer fiber optics; [Völkl et al., 1999](#)) can contribute to the measured phase difference. For this reason it is common practice to acquire a reference hologram, which is an empty hologram without the sample, acquired directly after the acquisition of the hologram with object information and using exactly the same illumination and imaging conditions. The phase image can be corrected for the camera distortions and lens aberrations by subtraction of the phase in the reference hologram ([Völkl et al., 1999](#)). Because the phase is measured in values between -2π and 2π , phase jumps will be present in the phase image if large phase gradients are present. To remove these jumps a so-called phase unwrapping algorithm is used to remove the phase jumps and obtain a continuous phase image. An unwrapped phase image is shown in [Figure 9.2\(f\)](#). Different unwrapping algorithms can be used.

Now the next question arises: what information is contained in the phase?

9.1.3 What do we measure in the absence of magnetic fields?

The phase change $\Delta\phi$ between an electron that passed through the sample and an electron that passed through vacuum is given by ([Mankos, Scheinfein, & Cowley, 1996](#))

$$\Delta\phi(\vec{r}) = C_E \int V(x, y, z) dz - \frac{e}{\hbar} \iint \underline{B}(x, y) d\underline{S} \quad (9.4)$$

where C_E is an interaction constant depending on acceleration voltage. For 200 keV electrons, the value of C_E is $7.29 \times 10^6 \text{ rad V}^{-1} \text{m}^{-1}$, $\underline{B}$ is the magnetic flux (or induction), and $\underline{S}$ is normal to the area mapped out by the trajectories of the electrons going from source to detector through the vacuum and the sample ([Midgley, 2001](#)). In the absence of magnetic information in the sample, this formula can be simplified to

$$\Delta\phi = C_E \int V(x, y, z) dz \quad (9.5)$$

so the phase change $\Delta\phi$ (between electrons that traversed the vacuum and electrons that traversed a specimen of thickness dz) can be directly related to the crystal potential $V(x, y, z)$ (in the absence of magnetic fields). For clarity it is useful to split the crystal potential $V(x, y, z)$ into two separate components, giving

$$\Delta\phi = C_E \int (V_0 + V) dz \quad (9.6)$$

where V_0 is the mean inner potential (MIP) of the crystal and V is the electrostatic potential. The MIP is the volume averaged electrostatic potential of a solid due to incomplete screening of the atomic cores, and is a property of the material under study. When the electron traverses the solid, an atomic core is never far away, and therefore the electron senses an average positive potential (Williams & Carter, 1996). The MIP is therefore a positive number. The electrostatic potential term V describes the potential as known from solid-state physics, determined by polarization, doping, strain, and surface charges. If we consider, for instance, a p–n junction in silicon (with doping concentrations below 10^{21} cm^{-3} ; Cooper & Dunin-Borkowski, 2013), the MIP is the same everywhere and the difference between Eqs 9.5 and 9.6 is not important because the only parameter influencing the phase change is due to doping contrast. However the distinction between Eqs 9.5 and 9.6 becomes important when we consider heterojunctions, as the two materials will most probably have a difference in MIP, which is added to the difference in potential over the junction, complicating a quantitative analysis of the phase image.

Diffacted electrons interact strongly with the crystal: a diffracted electron is directly in the Bragg condition to be re-diffracted back into the original beam, and so on. Due to these dynamic diffraction effects, the phase change of a dynamically scattered electron that passes through a specimen with thickness t cannot be understood using a simple formula but has to be calculated by solving the Schrödinger equation. However in medium-resolution electron holography, the specimen is tilted carefully off zone axis by approximately 4° to minimize diffraction contrast and the kinematic approximation is valid (Eqs 9.5 and 9.6). Diffraction contrast can complicate the analysis of NWs more than for 2D samples, because NWs can be bend either due to the growth, for instance the presence of heterostructures, and related strain, or due to dispersion of the thin NWs on another substrate, for example, a holey carbon grid, where the NW is bent on the grid by Van der Waals forces. If the NW is bent, the diffraction condition changes along the NW, and this will give rise to phase changes that are unrelated to the electrostatic potential.

9.1.4 Why bother?

As described, the measurement of the phase change by holography is sensitive to the electrostatic potential (change) in the sample, and obviously this is a parameter that can give us information about the 3D distribution of doping, polarization fields, strain, and surface charge with nm-scale spatial resolution in the sample under study, which is

undoubtedly useful. In this section I want to remind the reader very briefly of the basic equations underlying the electrostatic potential that can be found in any solid-state physics textbook, to avoid confusion.

What we measure in holography is both the MIP of a material as well as the electrostatic potential V , which is also just referred to as potential. It is often referred to as V_0 in microscopy textbooks (e.g., Williams & Carter, 1996) including the MIP ($V(x, y, z)$) above. In physics textbooks, this quantity is often referred to using the Greek ϕ symbol, referring only to V in Eqn 9.6. The relation between electrostatic potential V and potential energy E of a positive test charge q_0 is given by

$$E = q_0 V \quad (9.7)$$

if V and E are chosen to be zero at the same point. Now moving to semiconductors, we can define a relation between the electrostatic potential and the potential energy of an electron by

$$V = -\frac{E_i}{q} \quad (9.8)$$

where E_i refers to the intrinsic Fermi level (Sze, 1985), since this level is frequently used as a reference level when discussing extrinsic semiconductors. In an energy diagram of conduction (and valence) band we systematically plot the potential energy of the electrons (and holes, but the direction of the energy y-axis is inverted). From Eqn 9.8 we can now see easily that because of the negative charge of the electron, the potential profile is mirrored with respect to the potential energy, as represented graphically in Figure 9.3.

Why is it useful to remember the basic physics?

First of all because what we measure in holography, $V(x, y, z)$, is a superposition of the potential landscape in the sample and the MIP of the material itself (Eqn 9.6). If we consider a p–n junction in a single material, we will in principle only have a variation in the potential profile because the MIP of the material is the same everywhere. However, if we consider hetero-interfaces, such as GaN–AlN, then we will measure a superposition of the built-in potential and the difference in MIP of the materials. Now if the interface is not atomically sharp, this will have an effect both on the potential distribution and on the MIP variations, so obviously it becomes hard to obtain quantitative data. Furthermore, even for an atomically sharp interface, the reconstruction procedure will broaden the interface and therefore it is hard to separate the different effects. In fact the problems do not end here because obtaining a precise determination of the MIP is not obvious. Experimental measurements show a large dispersion in experimental MIP values, and the MIP can be calculated using different methods, which do not lead to exactly the same results. Also high doping concentrations can modify the MIP value, for instance, because the dopants are both in substitutional as well as interstitial positions, and are not all electrically active (Cooper & Dunin-Borkowski, 2013). Last but not least, several publications have observed an effect of particle size on the MIP value with a large spread in the data for gold

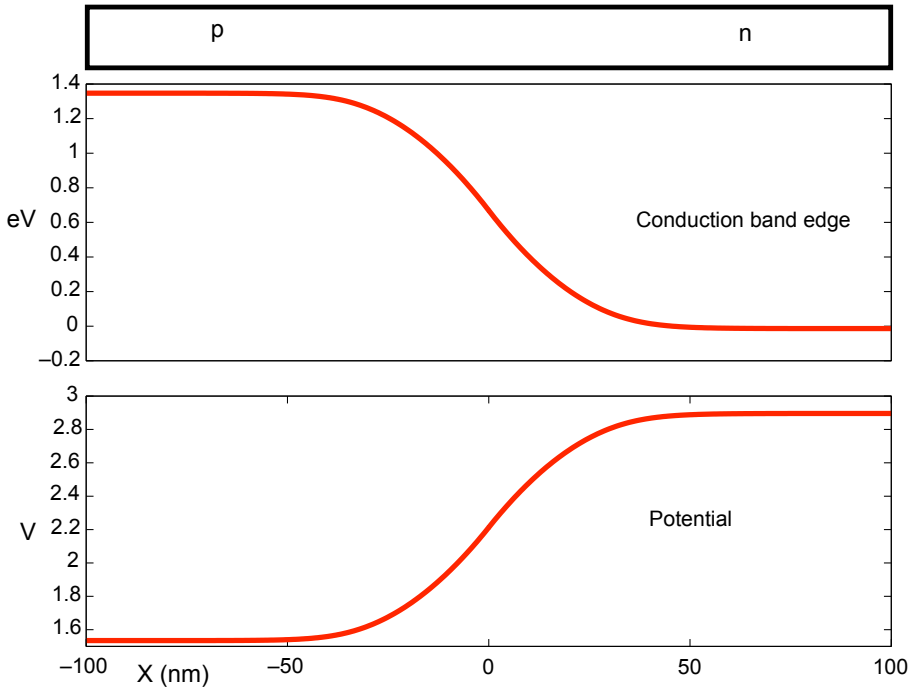


Figure 9.3 Example of the conduction band profile and corresponding potential profile in a p–n junction in GaAs.

particles, carbon nanotubes (CNTs), and silicon NWs, respectively (den Hertog, 2009; Ortolani, Houdellier, Monthieux, & Snoeck, 2011; Popescu et al., 2007). This effect is assumed to be associated with a redistribution of valence electrons of the surface atoms reducing the screening of the core, and is indeed stronger for gold than for CNTs, as no partially coordinated surface atoms are present in CNTs (Ortolani et al., 2011). To my knowledge the effect has not been reproduced satisfactorily in simulations.

In some cases holography is presented to give an image of the conduction band profile, which is the mirror image of the potential profile. Indeed it is very easy to mirror the phase image; all we need to do is take the other sideband in the holography reconstruction. However, this is not physically correct and this line of thought does not take into account that in fact we measure a superposition of potential profile and MIP. But as outlined before, for an analysis of a pure material in the low doping regime the results can be correct.

In semiconductors the measurement of the electrostatic potential can be used to gain access to active doping concentrations in the specimen. If a crystal is doped by a p-type dopant atom or n-type dopant atom, the location of the valence and conduction bands are modified with respect to the Fermi energy of the material. For this reason a potential difference is observed when going from the p- to the n-type material

(see Figure 9.3). This potential change is called the built-in potential V_{bi} (Sze, 1985) and is given by

$$V_{bi} = \frac{\kappa T}{e} \ln \left(\frac{N_A N_D}{n_i^2} \right) \quad (9.9)$$

where κ is the Boltzmann's constant ($1.380,658 \times 10^{-23}$ J/K), n_i is the intrinsic carrier concentration in silicon (9.65×10^9 cm⁻³; Sze, 1985), and N_A and N_D are the acceptor and donor concentrations, respectively. This formula can be used only in the absence of other charges, since their presence will also modify the location of valence and conduction bands with respect to the Fermi level in both p- and n-type materials and therefore the potential change over the junction will be different. The step-in phase that is measured over a p–n junction can therefore be related to the built-in potential and can be used in principle to measure doping concentrations quantitatively (Eqn 9.9). Obviously this potential change can also be influenced by internal fields due to spontaneous or piezoelectric polarizations (for instance, in nitride materials) and surface charges or traps.

9.2 Challenges with 2D samples

So far we have spoken about the theory of electron holography and the wonderful capabilities of this technique. Now it is time to come down to earth to face the challenges when dealing with real, imperfect samples, for the remainder of the chapter. For 2D samples, the focused ion beam (FIB) sample preparation has made excellent progress in electron holography possible, because it allows a very precise localization of the sample, which is more and more important with the downscaling of devices, and parallel-sided specimens without thickness variations can be easily obtained. However, FIB specimen preparation has one major defect: it creates a so-called dead layer, or electrically inactive layer, on the sample surface (Rau, Schwander, Baumann, Höppner, & Ourmazd, 1999). This layer is still crystalline, so it is measured when measuring the crystalline thickness of the sample, but it is not electrically active and its width depends both on doping concentration as well as sample preparation, the conditions used for the FIB milling (Cooper, 2006; Cooper et al., 2008, 2010). For this reason, the presence of the dead layer complicates quantitative analysis of doping concentrations. The solution to this problem is the use of *in situ* electrical biasing of the specimen in the TEM, as shown by Twitchett, Dunin-Borkowski, and Midgley (2002). By applying a reverse bias to the junction, the step in potential can be modified and a relation between the applied potential and the measured step in phase can be obtained. From the slope of this relation both the true built-in potential as well as the electrically active thickness can be obtained. In general, *in situ* electrical biasing appears to be a powerful method to eliminate the many possible artifacts that can appear in electron holography.

9.3 Nanowire sample preparation

The good thing about holography of NWs is that they do not need specific sample preparation to make them electron-transparent, which means that no artifacts related to thinning are present. However, NWs still have a surface that will alter their properties due to surface defects and traps, but at least these are inherent properties of the NW that we need to study and control anyway to eventually use the NWs in applications. The most common sample preparation of NWs for TEM is to break them off the growth substrate and disperse them on a TEM-compatible substrate, like a holey carbon grid, either mechanically or through dispersion in solution. For such samples in holography several difficulties arise:

- It can be difficult to orient the NW and minimize diffraction contrast because the NW is thin and also the preparation might have increased bending of the NW, increasing the influence of diffraction contrast.
- There might not be a suitable region of vacuum next to the NW, which we need for the reference wave because of the support or a too high NW density.

In my experience best results were always obtained on cleaved NW samples. The cleaving sample preparation of NWs is a relatively fast and manual process that does need only basic and cheap tools, and is described in detail in [den Hertog \(2009\)](#) and in the supporting information of [den Hertog et al. \(2009\)](#). This method makes it possible to obtain holograms of NWs that are still attached to the growth substrate; a global outline of such a sample is shown in [Figure 9.4](#). This sample preparation technique has several advantages:

- The NWs are not modified in any way — chemically, physically (for instance, by a solution), or mechanically (by bending).
- The specimen is electrically connected to the wafer, so artifacts due to charging are reduced ([Cooper et al., 2008](#)).
- The specimen is observed completely surrounded by vacuum and therefore not influenced by the structure of, for example, a carbon support film.

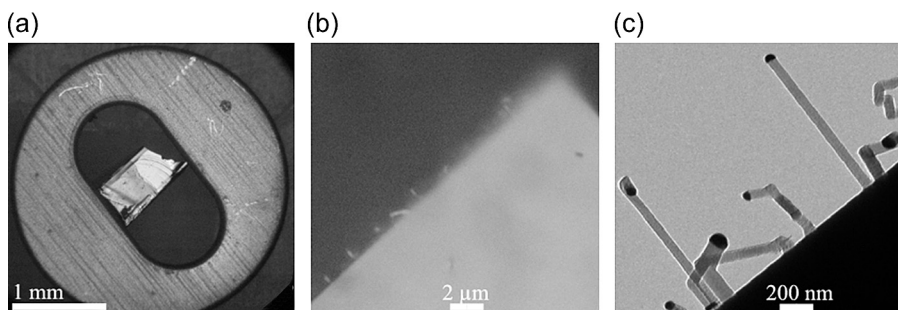


Figure 9.4 An example of a cleaved specimen. (a) Optical microscope image of the nanowire substrate attached to the TEM grid. (b) Optical microscope image showing the nanowires near the cleaved edge. (c) TEM BF image (Lorentz lens) showing the nanowires on the substrate.

- If the NWs are grown in epitaxy on the substrate, then all NWs on the substrate are oriented similarly with respect to the electron beam, which facilitates greatly the correct orientation of the specimen.
- The wedge edge can be used as a marker, allowing easy complementary study of the same unique nano-object using different (TEM) characterization techniques.

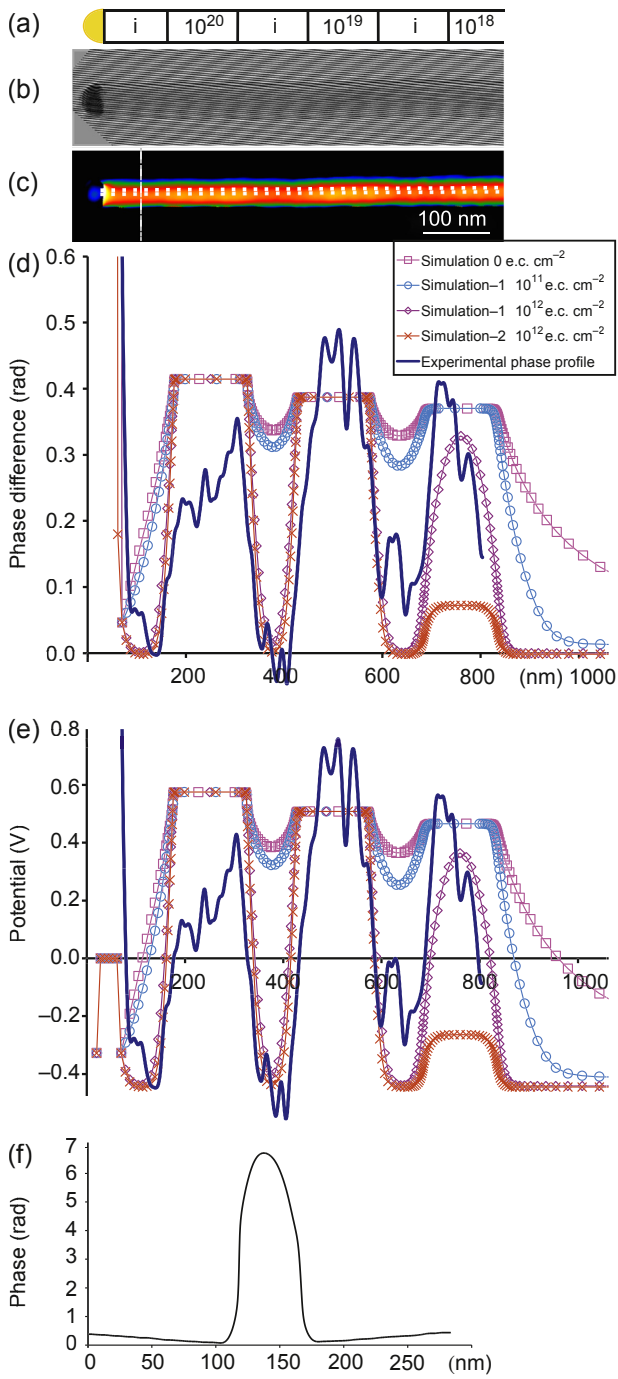
However, the method is difficult to use on NWs that grow very densely on the substrate. For nitride NW heterostructures, we have made a specific growth run where the NWs were grown on an Si post. The TEM sample was then prepared by cleaving and in this way free-standing nitride NW heterostructures can be studied in the cleaved sample geometry (den Hertog, Songmuang, & Monroy, 2013).

9.4 Literature on nanowires

Searching for literature on holography of NWs or nanoparticles (NPs), you will find that there is not as much literature as you might expect, given the possibilities of the technique. Yet in recent years this field has been developing. To my knowledge the first paper showing holography of relatively large NWs (diameter around 150 nm) was a study on core shell Ge NWs that could establish the MIP of both core and shell, evaluate the shape of the NW, and estimate the doping of the shell (Chung & Rabenberg, 2006). Then several holography papers in 2011 described hole accumulation in core shell Ge—Si NWs (Li et al., 2011) (which will be described in detail in the next chapter), the measurement of charge along a CNT bundle (Beleggia, Kasama, Dunin-Borkowski, Hofmann, & Pozzi, 2011), and electron holography—tomography of core shell GaAs—AlGaAs NWs where they could assess both the MIP of the core and shell and the 3D shape of the NW (Wolf, Lichte, Pozzi, Prete, & Lovergine, 2011). It was shown in Li et al. (2012) that polarization fields can be detected in ZnSe NWs at the zincblend—wurtzite interface, which will be described in the next chapter. Following on the work of Beleggia et al. (2011), counting of elementary charges on MgO NPs was shown in 2013 by Gatel, Lubk, Pozzi, Snoeck, & Hÿtch (2013). This method appears very promising and should allow the correlation of quantum transport phenomena with electron holography to establish both the physical effect of a single charge and its location with nm-scale precision.

9.5 Off-axis holography of semiconducting NWs

In this section two studies are shown of electron holography of semiconducting NWs. Off-axis medium-resolution electron holography was performed on an FEI Titan 80—300 working at 200 kV. The first study is about doping characterization in Si NWs and was earlier published in den Hertog (2009) and den Hertog et al. (2009, 2010). The second study is on characterization of polarization fields in GaN—AlN NW heterostructures, and was published in den Hertog et al. (2013).



9.5.1 Doping characterization in silicon NWs

Silicon NWs are highly studied for possible integration in future electrical and electro-optical devices. However, for many applications the doping profile of these nanostructures should be controlled at the sub-nm level. However, no measurements of the active dopant concentration within a thin nanostructure with a nm-scale spatial resolution have so far been demonstrated.

In this section the mean experimental results and interpretation using off-axis holography obtained on NWs with axially modulated doping are described and compared to potential simulations. Much more detail can be found in [den Hertog \(2009\)](#) and [den Hertog et al. \(2009, 2010\)](#). We end the section with a summary.

An example of dopant characterization in Si NWs is shown in [Figure 9.5](#). The NW sample was grown by IBM Zurich ([den Hertog et al., 2009](#)), where the doping concentrations were estimated from transport measurements ([Björk, Knoch, Schmid, Riel, & Riess, 2008](#); [Björk, Schmid, Knoch, Riel, & Riess, 2009](#); [Schmid et al., 2009](#)), and was prepared for TEM analysis using the cleaving technique ([den Hertog, 2009](#); [den Hertog et al., 2009](#)).

[Figure 9.5\(a\)](#) shows a schematic illustration of a NW with the hemispherical gold tip on the left side, and axially *n*-doped segments are shown with phosphorus *n*-doping concentrations of 10^{20} , 10^{19} , and 10^{18} at cm^{-3} going from left to right alternated with intrinsic regions that we assume to have a light *p*-doping of 10^{15} at cm^{-3} . All sections were grown to have a length of 150 nm. [Figure 9.5\(b\) and \(c\)](#) show the NW hologram and the reconstructed phase image with enhanced contrast levels for better visibility. A phase profile was obtained along the dotted horizontal line and is shown in [Figure 9.5\(d\) and \(e\)](#), with the *y*-scale in radians or volts (using [Eqn 9.5](#)), respectively. The phase image and profile clearly reveal the structure of the silicon NW showing three segments of higher-phase shift that correspond to the doped segments, alternated by intrinsic segments. A closer look at the phase profile shows that the peaks do not have a decreasing intensity going from the top of the NW to the right, as would be expected for decreasing doping concentrations. In particular, the peak closest to the tip and related to the highest *n*-doping shows a markedly reduced phase shift, which suggests that the proximity of the Au tip might affect the potential distribution. An explanation could be that carriers present in the first doped region flow into the gold

Figure 9.5 (a) Schematic of a nanowire that contains three *n*-doped (phosphorus) regions of varying doping concentration: 10^{20} , 10^{19} , and 10^{18} at cm^{-3} . The doped regions are separated by intrinsic regions. All segments are ~ 150 nm long. (b) Hologram of the nanowire. (c) Phase image with amplified color scale. (d) Phase profile (solid line) made at the dotted line, averaged over 3.5 nm. Simulations of the phase profile at the center of this structure with zero charge at the wire–oxide interface ($\square$), with -1×10^{11} e.c. cm^{-2} charge at the interface ($\circ$), with -1×10^{12} e.c. cm^{-2} charge ($\diamond$), and with -2×10^{12} e.c. cm^{-2} charge ($\times$) are plotted for comparison. The phase difference was obtained from simulation by multiplying the potential with t and C_E ([Eqn 9.5](#)). (e) Potential profiles made using the same data as in (d) and [Eqn 9.5](#). (f) Phase profile obtained along the dashed line in (c). The crystallographic growth direction of the nanowire was $\langle 111 \rangle$.

catalyst or create a buildup of charge near the catalyst interface, due to the difference in work function, thereby effectively reducing or masking the dopant-related potential in the first doped region.

The phase and potential profiles in [Figure 9.5\(d\) and \(e\)](#) are compared to simulated profiles performed for a cylindrical NW with different negative charge quantities present at the oxide silicon interface that were varied from 0 to -2×10^{12} e.c. (electron charges) cm^{-2} and converted from volts to radians using the projected potential and [Eqn 9.5](#) (the NW diameter is 56 nm). The simulations show that without charges in the oxide, the expected phase step will be below 0.1 rad between each of the alternating segments, due to the large depletion width in the intrinsic region ($\sim 1 \mu\text{m}$; [Sze, 1985](#)). However, the phase signal in the experimental data is much larger than suggested from simple calculations and corresponds well to simulations that use a sheet charge at the oxide interface of -1×10^{12} e.c. cm^{-2} , which is in excellent agreement with the charge density at the oxide–SiNW interface deduced from transport measurements ([Björk et al., 2009](#)). Due to the negative charges at the oxide interface, the electrons are repelled from the intrinsic segment, effectively reducing the depletion width to around 50 nm. In accordance the visibility of the lowest doped segment (10^{18} at cm^{-3}) depends very sensitively on the amount of charge present at the oxide interface, owing to the increased depletion width. It should be noted that the region with 10^{18} at cm^{-3} doping was not equally well visible in all observed NWs. The regions with 10^{20} and 10^{19} at cm^{-3} doping were visible in all observed NWs, but the 10^{19} at cm^{-3} region systematically caused a larger step-in phase.

In [Figure 9.5\(f\)](#), a vertical phase profile across the NW is shown, as indicated by the dashed vertical line in [Figure 9.5\(c\)](#). Clearly the phase signal increases in the vacuum when going away from the NW, indicating electric fields in the vacuum that could be caused by the negative charge present in the oxide, in support of the presence of negative surface charges. Comparison of the experimental phase gradient with simulated phase gradients in the vacuum as a function of interface charge quantity allows an independent estimation of the charge density of -1×10^{12} e.c. cm^{-2} . However, this correlation is not sufficiently precise to decouple the effect of surface charge from the effect of doping concentration ([den Hertog et al., 2010](#)).

It is clear from the present results that it is difficult to derive quantitative dopant concentrations from the phase profiles extracted across highly doped regions, as the fluctuations in the experimental phase profiles are relatively large compared to the differences in simulated phase change. Because the phase sensitivity of our experimental setup is approximately 0.01 rad ([Cooper, Truche, et al., 2007](#)), the observed noise on the experimental data appears to be intrinsic to the specimen and is probably mostly due to a rather homogeneous distribution of Au clusters on the NW surface with a size below the spatial resolution of the measurement that is around 10 nm, which adds a source of background noise that can locally increase the phase shift by 0.1–0.2 rad ([den Hertog et al., 2008, 2009](#)). Also, the phase change over the region with the highest doping, 10^{20} at cm^{-3} , is reduced with respect to the phase change over the region with the lower doping, 10^{19} at cm^{-3} . However, the data allow estimation of a negative interface charge density of -1×10^{12} e.c. cm^{-2} and spatial localization of the junction with 10 nm spatial resolution.

We have shown that the experimental data agree well with simulations where negative charges are present at the silicon–oxide interface. Several hypotheses can explain

the origin of such negative charges. The simulation assumes that fixed charges are present at the oxide interface. In reality there are three possible contributions to the charge density at the oxide interface (Nicollian & Brews, 1982): (1) the fixed-oxide charges in the oxide, (2) interface-trapped charges, and (3) electron beam-induced oxide-trapped charges (Fazzini, Merli, Pozzi, & Ubaldi, 2005; Nicollian & Brews, 1982), due to the generation of electron hole pairs by the high-energy electron beam (Houben, Luysberg, & Brammer, 2004). The estimated number of charges at the oxide interface of -1×10^{12} e.c. cm^{-2} is in excellent agreement with the value found by transport measurements (Björk et al., 2009). Transport measurements (Björk et al., 2009) do not make it possible to distinguish fixed charges from interface-trapped charges; however, it is generally accepted that this order of magnitude of charge densities is due to interface traps (Schmidt, Senz, & Gösele, 2007). Furthermore, interface traps seem physically more realistic because the charges are supplied by the dopants and therefore a dipole is present and the object is globally neutral. Interface traps can be either acceptor or donor-type, depending on the position of the Fermi level with respect to the valence and conduction band (Schmidt et al., 2007; Sze, 1985). Therefore negative charges would be expected mostly at the surface of the n-doped segments (Björk et al., 2009; Schmidt et al., 2007; Sze, 1985). However, the comparison of holography experiments and simulation shows that negative charges are also present at the surface of the intrinsic regions. This could be due to the complicated nature of the NW surface. The crystal planes present are {111}, {112}, and {100} (den Hertog et al., 2007; Ross, Tersoff, & Reuter, 2005), partially different from the well-studied case of interface traps at the silicon–silica interface of {100} and {110} oriented silicon wafers. Another possibility is the influence of the electron beam on the occupation level of acceptor-type interface trap states.

It seems likely that in the experiment such interface traps can be negatively charged due to the influence of the electron beam in the lightly p-doped intrinsic region, since it was found by simulations (Houben et al., 2004) that especially the minority carrier concentration is modified by the electron beam during the holography experiment. Furthermore, an influence in the acquired potential map is expected only for lowly doped silicon ($\leq 10^{17}$ at cm^{-3}). Indeed this effect could modify the observed potential profile in the intrinsic regions. Another possible explanation based on these simulations (Houben et al., 2004) could be a positive charging of the sample due to secondary electron emission creating an increased p-type-like doping under the electron beam, which would also reduce the depletion width. On the other hand, this last explanation is not coherent with the observation presented in Figure 9.5(f) indicating a negative charging of the sample.

The NWs in this sample did not contain thickness variations; the NW surface is faceted and a homogeneous distribution of gold clusters is present, consistent with Ross et al. (2005) and den Hertog et al. (2008). A schematic illustrating the doping concentrations, the phase image with amplified color scale, and the extracted phase profile across the NW is shown in Figure 9.6 of the first intrinsic and doped sections of an NW, to illustrate clearly that no thickness variations are present that could cause the observed phase variations. Furthermore, phase variations in the vacuum around the doped regions were sometimes observed (den Hertog et al., 2010), which is an independent proof that indeed doping contrast is observed and

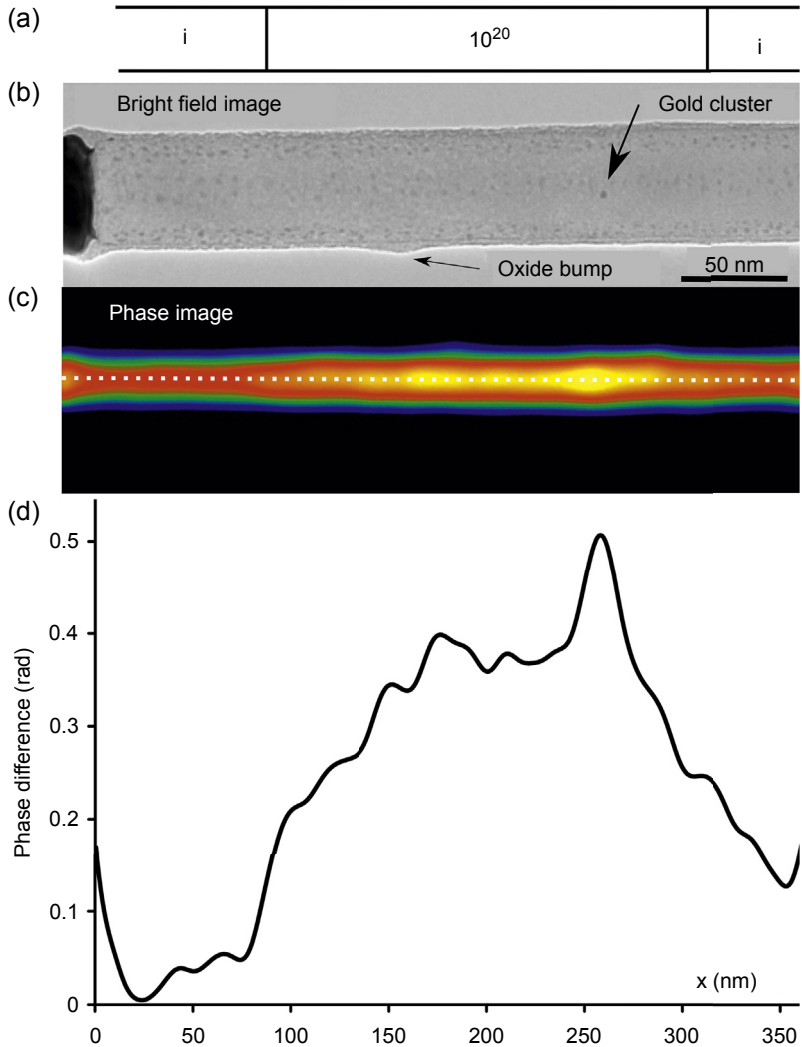


Figure 9.6 (a) Schematic of a detail of a nanowire. (b) Bright field image. No thickness changes were observed and gold clusters are present on a faceted surface. A larger gold cluster and a small thickness change of the oxide shell can be observed. The crystallographic growth direction of the nanowire was $\langle 111 \rangle$. (c) Phase image with amplified color scale showing one doped region. (d) Extracted phase profile across the phase image shown in (c).

not a thickness-related artifact that could also create phase jumps. In another NW sample, thickness variations were indeed present at the $n-i$ junction (den Hertog et al., 2009; den Hertog, 2009), which is not convenient as we know from Eqn 9.5 that an increase in thickness will also create a phase change. This complicates the analysis of the phase signal, but we could show that only part of the observed phase signal

can be attributed to the thickness variations, and the major part of the phase change can be attributed to doping contrast.

In summary we have shown that electron holography can be used to map active dopants qualitatively in silicon NWs as thin as 60 nm with 10-nm spatial resolution, as well as the position of the junction. Experiment and simulation demonstrate that doping concentrations of 10^{19} and 10^{20} cm^{-3} can be measured with a detection threshold of 10^{18} cm^{-3} with respect to intrinsic silicon. Charges near the wire–oxide interface have a large influence on the measured potential and can be estimated by comparison of experimental data with simulations to be $-1 \times 10^{12} \text{ e.c. cm}^{-2}$. On the other hand, due to numerous artifacts only qualitative data can be obtained on these NWs and several hypotheses are possible to explain the origin of the surface charges. Also the abruptness of the junction can be estimated (den Hertog, 2009; den Hertog et al., 2009). Phase modulations in the vacuum at the side of the NW, so-called fringing fields, were observed and compared to simulations (den Hertog et al., 2010).

Quantitative measurement of the doping concentration in nanostructures seems possible in the near future if variations due to gold clusters and faceting can be removed. An improved experiment to extract quantitative dopant concentrations from semiconductor samples would be to bias the specimen *in situ* in the TEM (Twitchett, Dunin-Borkowski, Broom, & Midgley, 2004). The electrical connections to the NW would also remove the carriers generated by the electron beam more effectively (Cooper et al., 2008; Cooper, Twitchett-Harrison, et al., 2007).

9.5.2 Characterization of polarization fields in GaN–AlN NW heterostructures

III-nitride semiconductors, with their direct bandgap, flexibility for band engineering, and capability of operating in extreme environments, are promising materials for single-NW devices, for instance high-resolution chemical sensing or high-spectral-contrast photodetectors. A particularity of nitride materials is the very strong polarization-related internal electric field present in heterostructures, which can be assessed through its effect on optical or electrical properties. A direct measurement of the internal electric field profile is more challenging but could in principle be realized by off-axis electron holography. Holography of nitride materials was already reported (Cai & Ponce, 2002; Cai, Ponce, Tanaka, Omiya, & Nakagawa, 2001; Carthney, Ponce, Cai, & Bour, 2000; Cherns & Jiao, 2001; Fischer, Sun, Ponce, Songmuang, & Monroy, 2012). In addition to the technical difficulties to measure the field distribution, these direct measurements are necessarily perturbed by the superposition of information on surface depletion due to surface states and by the effect of strain on the internal field distribution. Taking these phenomena into account is critical to understand the physical properties of such nanostructures. Here we use medium resolution off-axis electron holography to measure the projected potential in GaN/AlN NW heterostructures and compare our experimental results with 3D potential simulations to discriminate the 3D field distribution and the effect of surface charge.

For this study, GaN NWs containing a 10-period GaN/AlN (7 nm/7 nm) superlattice, followed by 30 nm of GaN and 30 nm of AlN, were grown on Si(111) patterned

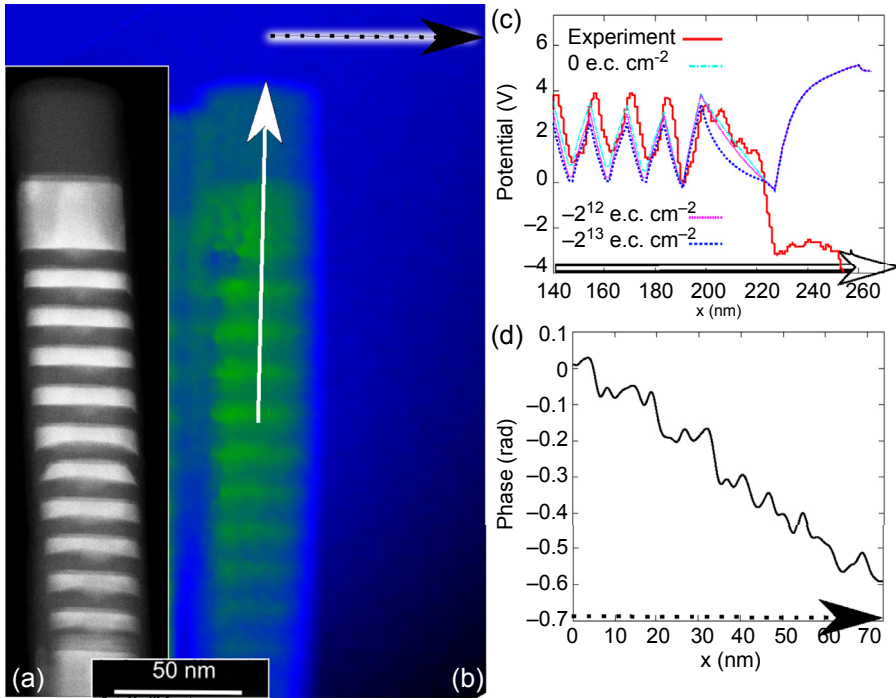


Figure 9.7 (a) HAADF STEM image of a GaN/AlN NW heterostructure. (b) Phase image of the same NW. (c) Potential profile obtained from the phase along the vertical white arrow compared with three simulated profiles without surface charge, including a surface charge density of -2×10^{12} e.c. cm^{-2} charge and -2×10^{13} e.c. cm^{-2} charge. (d) Phase profile in the vacuum obtained along the horizontal black dotted arrow. The crystallographic growth direction of the nanowire was $[000\bar{1}]$.

From [den Hertog et al., 2012](#).

pillars. Details of the NW growth and TEM sample preparation using the cleaving technique can be found in [den Hertog et al. \(2013\)](#).

Previously we have demonstrated that GaN NWs are hexahedral structures with relatively flat $\{10\bar{1}0\}$ *m*-plane sidewall facets, and they exhibit N-polarity, as identified by annular bright field and high-angle annular dark field scanning transmission electron microscopy (HAADF STEM) ([den Hertog et al., 2012](#)). As off-axis holography is sensitive to the projected potential, we expect to observe the effect of the polarity on the potential in the structure. [Figure 9.7\(a\)](#) presents a HAADF STEM image of a GaN/AlN heterostructured NW, where the brighter regions correspond to the GaN layers. The axial superlattice is enveloped by an AlN shell arising from the lateral growth during the deposition of the AlN sections. As a result of the elevated growth temperature, a certain interdiffusion is observed at the interfaces. This phenomenon is particularly important when starting the growth of AlN on GaN, giving rise to a graded interface, which extends along

about 1.5 nm. Figure 9.7(b) shows the phase image obtained by off-axis electron holography, tilted several degrees off the Si [112] zone axis. The fringe spacing was 1 nm, giving a spatial resolution in the reconstructed phase image of around 3 nm. The various GaN and AlN regions can be clearly resolved. As GaN and AlN do not have the same MIP ($\text{MIP}_{\text{GaN}} = 16.8 \text{ V}$ and $\text{MIP}_{\text{AlN}} = 14.2 \text{ V}$; Kruse, Schowalter, Lamoen, Rosenauer, & Gerthsen, 2006), it is important to realize that in this case Eqn 9.6 is the relevant equation where the electrostatic potential V reflects the combined effects of spontaneous and piezoelectric polarization and surface charges. However, separation of MIP and potential contributions could not be realized for these data because of the intermixed regions at the GaN–AlN interface. In Figure 9.7(c), a projected potential profile is obtained from the phase image in Figure 9.7(b) along the white vertical arrow using Eqn 9.5 and the measured NW thickness. The experimental potential profile is compared to three simulated potential profiles obtained from projected 3D simulations of an NW structure with the layer sequence of the sample in Figure 9.7(a), including surface charge densities ranging from 0 to $-2 \times 10^{13} \text{ e.c. cm}^{-2}$, which is one order of magnitude higher than a value from the literature (Bertelli et al., 2009). These simulations take into account the NW hexagonal cross-section with m sidewall facets, with the dimensions extracted from our STEM measurements, including the presence of the AlN shell and the alloyed regions that were assumed to have a composition of $\text{Ga}_{0.5}\text{Al}_{0.5}\text{N}$. The strain distribution is calculated to minimize the elastic energy in the system considering a free-standing NW in vacuum. The calculation of the 3D potential profile takes into consideration the local variations of the bandgap due to strain, as well as the 3D internal electric field induced by spontaneous and piezoelectric polarization. However, our simulations do not include the variation in MIP between GaN and AlN; thus, the experimentally obtained potential profile was shifted along the y -axis to allow comparison to the simulated profiles. We verified that the step in phase over the AlN top region is consistent with the thickness and the MIP of AlN. For the studied NW, the expected change in potential when going from a GaN to AlN region due only to the variation in MIP would be around 0.8 V, if we assume the NW diameter of 44 nm is roughly equal to the thickness. The experimentally measured potential change at the GaN/AlN heterointerfaces is much larger than the calculated 0.8 V, indicating that indeed the measurement is sensitive to the electric field. However, in the studied NWs there are composition gradients at the interfaces, creating also a gradient in the MIP. Therefore, we cannot provide a quantitative assessment of the interface charge in this structure, but quantitative measurements are feasible in structures with abrupt interfaces and homogeneous alloy composition.

Making a qualitative analysis, the experimental profile is comparable to the simulated profiles and consistent with the N-polarity of the NW. Interestingly, the internal field is so strong that the surface charge does not have much influence on the projected potential, in strong contrast to the results obtained on Si NWs presented previously (den Hertog et al., 2009, 2010), even though the highest value of the surface charge used in the simulation is higher than experimentally measured on a clean GaN surface (Bertelli et al., 2009). On the other hand, the measurement at the AlN top region presents a deviation from simulations, which might be due to charging of the NW under

the electron beam. To investigate charging issues, we display in Figure 9.7(d) a phase profile in the vacuum at the side of the NW along the black horizontal dotted arrow in Figure 9.7(b). Going away from the NW, the phase decreases, indicating a positive charging of the NW (den Hertog et al., 2010). This could explain the lowering of the potential in the AlN top region. In summary, we have shown the first results of holography of GaN/AlN NW heterostructures, compared to theoretical calculations. We confirm the N-polarity of the NW and observe a positive charging of the sample under the electron beam. Comparison with simulated profiles does not allow setting a value on the surface charge of the NW. We have described some of the challenges that have to be met to allow quantitative field mapping in nitride NW heterostructures. In general, it is clear that a stable and high-performance microscope is indispensable for the study of such nano-objects as well as suitable sample preparation.

9.6 Conclusion and perspectives

If this chapter was useful, you should be convinced at this point that electron holography is a very powerful technique, sensitive to many different parameters in the specimen. This is also the reason why it is so difficult to obtain quantitative results using holography: often the phase signal contains contributions from different effects. The phase signal can contain contributions from local MIP variations due to defects, boundaries, strain, charged surface states, surface reconstruction and absorption, doping, polarization fields, interface segregation and interdiffusion, mobile charges compensating internal fields, thickness variations, contact potentials, beam-induced charging, and diffraction contrast (Lichte et al., 2013). To tackle this problem one option is to use complementary TEM techniques to obtain additional information to allow a better interpretation of the holography data; an example is Cooper & Dunin-Borkowski (2013), where complementary HAADF STEM in combination with strain analysis was used to separate contributions from the doping to the MIP and the electrostatic potential. However, *in situ* biasing experiments, as shown in Twitchett et al. (2002), appear an even more promising method to effectively separate electrostatic effects from other influences on the phase change. Lately there is a lot of development in TEM sample holders to allow *in situ* experiments in the TEM, like *in situ* biasing, heating, and indentation. For NWs, *in situ* biasing combined with holography was shown in He, Cho, Jung, Picraux, & Cumings (2013), where Si NWs with a p–n junction were contacted using a movable Pt tip, which is described in more detail in the next chapter. Unfortunately, it was shown that using this type of contact approach, no ohmic contact of good quality was obtained on the NW, but a Schottky contact with very high contact resistance. Therefore the applied potential could not penetrate into the structure to reverse bias the p–n junction in the NW. Also, using a tip to contact the NW will also slightly bend the NW and therefore add both strain as well as diffraction contrast, which could complicate the data analysis. *In situ* biasing of NWs is therefore very promising, but fabricating the good sample geometry that will not interfere with the holography experiment (for instance, charging under the beam), with good quality ohmic contacts, remains the main challenge.

9.7 Further reading

More information on electron holography in general can be found in [Midgley \(2001\)](#), [Völkl et al. \(1999\)](#), and many papers by H. Lichte and his group. Discussions on fringing fields in the vacuum can be found in [Twitchett et al. \(2002\)](#); [Beleggia, Cardinali, Fazzini, Merli, & Pozzi \(2008\)](#); and [Fazzini et al. \(2005\)](#). The problems with FIB sample preparation and the dead layer are well studied in several papers by D. Cooper. For more information on electrostatic fields, one should refer to the work of G. Pozzi. More work and microscopy groups working on electron holography are described in the next chapter.

Acknowledgements

I thank all of my coworkers on the different papers at the base of this chapter: Jean-Luc Rouviere, Rudeesun Songmuang, Thierry Fournier, Bruno Fernandez, Eva Monroy, Heinz Schmid, David Cooper, Mikael T. Björk, Heike Riel, Pierrette Rivallin, Siegfried Karg, and Walter Riess. Special thanks to David Cooper for teaching me holography and help on the microscope. I thank Martial Duchamp for proofreading of the chapter and the European Community and French ANR for funding.

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Electrical characterization of semiconductor nanowires by scanning-probe microscopy

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10.1 Introduction

The structure of a semiconductor crystal is spatially periodic, and this translational symmetry leads to the existence of an electronic band structure and phonon dispersion branches that give to the crystal its physical properties. However, when the size of the crystal shrinks, the contribution of the atomic layers at the surface can no longer be neglected and surface effects have to be carefully considered in the description of the crystal's physical properties. This is particularly true for semiconductor nanowires, which can be considered as one-dimensional objects with typical lengths of the order of a micrometer and diameters below 100 nm.

A wide range of techniques exists to characterize the surfaces of semiconductor materials. These techniques consist of imaging and diffraction methods to determine the structural properties of a semiconductor sample, and of spectroscopic methods to reveal its electronic structure, chemical composition, and chemical reactivity. However, most experimental techniques rely on the interpretation of indirect methods of investigation, which involves the integration of data over a large area, making the study of scattered semiconductor nanowires difficult. Due to its ability to image at the nanoscale, scanning tunneling microscopy (STM) encompasses both types of methods: it provides the morphology of a single semiconductor nanowire and a detailed picture of its surface; in addition, since the tunneling current inherently contains information about the local density of states of the sample, it also makes it possible to measure the nanowire electronic properties. Further, STM offers the unique advantage of obtaining these physical and chemical properties on an atom-by-atom basis. One of the first works to demonstrate the benefits of STM in the study of semiconductor nanowires was achieved for H-passivated silicon nanowires, where the nanowire sidewalls were imaged at the atomic resolution and the bandgap was measured with tunneling spectroscopy (Ma, Lee, Au, Tong, & Lee, 2003). Since then, scanning-probe microscopy has been widely used to improve our understanding of nanowire physical properties.

In this chapter, the operating principles of the scanning tunneling microscope are first discussed and then followed by a description of the existing preparation methods

to get access to the nanowire surface properties. Description of STM studies performed with Si or III–V semiconductor materials are given to highlight the importance of the nanowire surface in the growth dynamics of the nanowire and in the pinning of the Fermi level. We will show that STM is an ideal technique not only to observe the surface of individual nanowires with an atomic resolution, but also to probe their electronic properties. Finally, additional capabilities can be added to the scanning tunneling microscope, for example, to probe transport properties. As described in the last section, the use of multitip STM makes measurements of the conductivity through semiconductor nanowires quite attractive in order to evaluate the nanowire potential in optoelectronic devices.

10.2 Instrumentation

10.2.1 Basic principles of scanning tunneling microscopy

STM relies on the tunneling effect between a sharp metallic tip and a conductive sample, where electron waves incident on a potential barrier with finite height and width penetrate into this classically forbidden region of space. As electron tunneling decays exponentially with the barrier width, this process is relevant for a tunneling junction thickness of less than a few nanometers. However, without a voltage applied between both electrodes, there is no measurable current, because electrons tunnel equally from the tip to the sample and vice versa. Setting a voltage difference across the junction allows the tunneling current to flow, and such a current provides an outstanding probe to study the sample surface (Figure 10.1(a)). Indeed, by clamping the tip at the end of a scanner consisting of piezoelectric actuators, the tip can be displaced to change the

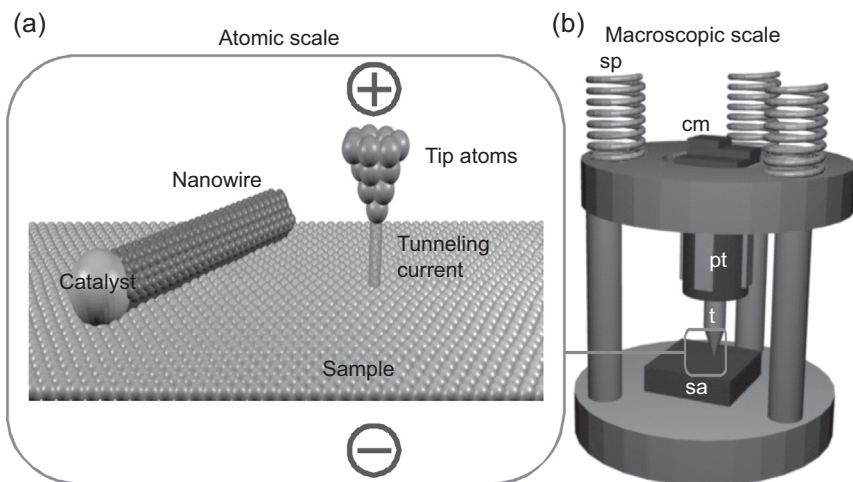


Figure 10.1 Schematic diagram of a scanning tunneling microscope (a) at the scale of the tunneling junction and (b) at the macroscopic scale where the different components are labeled as follows: sample (sa), tip (t), piezoelectric scanner (pt), coarse motor (cm), spring (sp).

width of the tunneling junction, as well as to scan back and forth over the surface of the sample. While variations of the tip–semiconductor surface distance makes it possible to probe the potential barrier of the junction (Avouris, Lyo, & Hasegawa, 1993; Chen & Hamers, 1991), moving the tip across the surface provides a map of the current intensity as a function of the tip position over the surface. As surfaces may be rough, a feedback circuit is generally used to keep the tunneling current constant by adjusting the tip position, in order to avoid any mechanical contact between the tip and the surfaces. In such a way, the spatial variations of the tip position, which are measured through the error signal of the feedback loop, reveal the morphology of a surface with a spatial resolution that can reach the atomic scale (Binnig, Rohrer, Gerber, & Weibel, 1982; Binnig, Rohrer, Gerber, & Weibel, 1983; Feenstra & Fein, 1985).

However, the tunneling current contains more information than just the surface morphology. For common metallic samples, electronic states are uniformly distributed near the Fermi level. But for semiconductor samples and in particular semiconductor nanowires, the tunneling current strongly depends on the local electronic structure of the sample. A direct visualization of spectroscopic information can be obtained by imaging surfaces with different voltages, which correspond to energy windows where different electronic states contribute to the tunneling current (Feenstra, Stroscio, & Fein, 1987; Stroscio, Feenstra, & Fein, 1987). When the metal tip is positive with respect to the semiconductor surface, occupied states corresponding typically to valence band states in the semiconductor contribute to the tunneling current, once the Fermi level of the tip is positioned below those states. Alternatively, when the metal tip is negative with respect to the semiconductor surface, electrons can tunnel from the tip states into the unoccupied states or conduction band states of the semiconductor surface, as soon as the tip Fermi level becomes aligned with those states. By measuring the dependence of the tunneling current on the applied voltage, an I – V characteristic can thus reveal the width of the semiconductor band gap for the surface or even the bulk, if the surface is passivated. It can also yield the spectral position of bands of surface states and bulk states that decays smoothly into the potential barrier.

10.2.2 Design considerations

Measurable tunneling currents usually range from tens of femtoamperes to hundreds of nanoamperes, depending on the width of the tunneling barrier and the conductivity of the sample. In order to achieve appropriate tip–sample separations, actuators, consisting of piezoelectric ceramics that expand or contract almost linearly with the voltage applied across the ceramics, are required to move the tip with a precision of the order of picometers. PZT-4D or 5H [$\text{Pb}(\text{Ti}, \text{Zr}, \text{O}_3)$] are examples of piezoelectric ceramics found in the scanners of the microscope. Their piezoelectric charge constant corresponds to a mechanical deformation of a few angstroms when a voltage of 1 V is applied at room temperature. The deformation amplitude is thus relevant to move a tip at the nanoscale under moderate bias. Actuators can consist of simple piezoelectric bars, assembled into a tripod scanner, but piezoelectric tubes (labeled “pt” in Figure 10.1(b)) are generally preferred, as their geometry gives more compact and

rigid scanners, where the outer wall electrode is typically split into four sections for X and Y motion, the inner wall electrode being dedicated to vertical Z motion.

Although the scanners exhibit mechanical deformations that allow the tip to be moved vertically back and forth from a semiconductor nanowire within a few micrometers, this range of separations is small in comparison with the macroscopic distances that exist when the sample and tip are transferred onto the microscope head. Additional drivers are thus required to perform the coarse motion (labeled “cm” in Figure 10.1(b)) and locate a nanowire at the surface of a sample. They may consist of piezo-drivers (stick-slip devices or clamped-step devices such as the inchworm), electrostatically clamped feet (louse walker) (Binnig & Rohrer, 1982), or more simply screws based on lever, gear, or spring reduction mechanisms (Demuth, Hamers, Tromp, & Welland, 1986; Drake et al., 1986; Pashley, Haberen, & Friday, 1988).

The precision required to maintain the tip above the semiconductor surface is also quite small in comparison to the amplitude of environmental vibrations, such as floor vibrations, which typically range from 0.1 to 1 μm . As a result, the reduction of mechanical and acoustic vibrations imposes stringent conditions on the rigidity of the microscope and the performances of the vibration isolation stage (Pohl, 1986). As the study of semiconductor nanowires is usually performed in ultra-high vacuum (UHV) because the nanowire surfaces are generally not inert, the central part of the microscope is damped with soft springs (labeled “sp” in Figure 10.1(b)), to mechanically decouple it from the UHV chamber that bears the microscope. The viscous damper can be achieved with the action of eddy currents induced by permanent magnets in copper plates, which surround the microscope head.

Similarly to the care applied to the mechanical design of the microscope to reach atomic resolution, the electronics that measure the current and control the scanner require sub-angstrom accuracy. The essential parts of the electronics are the feedback electronics and a circuit that controls the X and Y motion of the scanner. In the feedback electronics, the current is first amplified and converted into a voltage by a current-to-voltage amplifier, and then compared to a reference signal, before passing through a logarithmic amplifier in order to linearize the system response. The regulation is performed by using a proportional and/or integral feedback. A “sample and hold” amplifier is generally inserted in front of the proportional and integral amplifiers to allow the opening of the feedback loop and the acquisition of spectroscopic measurements such as I versus V and I versus Z characteristics.

10.2.3 Sample preparation

In air, most metallic and semiconductor surfaces are covered by a thin insulating layer that prevents stable tunneling conditions. In contrast, UHV corresponds to pressures lower than 10^{-9} Torr. Such low pressures allow delaying the time required to build up a monolayer of adsorbates, corresponding typically to a few 10^{14} adsorbates per cm^2 . For example, when the pressure is 10^{-10} Torr and assuming a semiconductor surface with a sticking coefficient of unity, almost 3 h are available for the characterization of a clean and well-ordered surface. Therefore, the surface analysis of nanowires usually required their observation in a UHV environment.

In order to make the nanowire characterization effective, different methods exist to clean the nanowire sidewalls. Wet chemical methods for surface passivation of semiconductor materials work, but with limited success. In particular for III–V materials (Seker, Meeker, Kuech, & Ellis, 2000), atomically resolved STM measurements are difficult, because the surfaces often become rough and do not have a very stable or crystalline character. As a result, several *in situ* surface treatments have been reported to clean and protect the surface structure of semiconductor nanowires from the oxidation in air, as shown in Figure 10.2(a). The first one corresponds to a rapid thermal annealing (RTA) of the nanowires, where a sufficiently high temperature enables the desorption of the oxide layer. This process has been successfully applied to remove the oxide layer at the surface of Si nanowires (Xu et al., 2010). By directly passing an electrical current through the Si substrate that was used to grow the nanowires, a temperature of 800 °C, measured on the substrate, allows the reaction of SiO₂ with underlying Si atoms on the nanowire sidewalls. The reaction product yields SiO species, which vaporize and leave an oxide-free surface. *In situ* Auger measurements showed that the oxygen peak disappeared after annealing, while the morphology of the heated nanowires observed with electron microscopes was found to be similar to the ones observed before RTA, indicating that the thermal treatment did not change the overall morphology of the nanowires.

However, the RTA process is not suitable for III–V semiconductor materials, because a high temperature causes a loss of the chemical species of the group V elements from the semiconductor surfaces, resulting in the surface decomposition and the formation of clusters consisting of group III elements (Vitomirov et al., 1992). An alternative surface preparation technique to produce clean and undamaged surfaces relies on an atomic hydrogen cleaning method (second scheme in Figure 10.2(a)). Indeed, etching the oxide layer of III–V semiconductor surfaces can be achieved with atomic hydrogen, while maintaining the materials at relatively high temperatures (Kikawa, Ochiai, & Takatani, 1994; Veal & McConville, 2000). This method has been shown to be successful for cleaning the surfaces of InAs and GaAs nanowires. For InAs nanowires, it was found that reasonably broad temperature range and annealing times (350–400 °C, 3–30 min) existed for obtaining clean and well-defined crystalline surfaces (Hilner et al., 2008). As to GaAs nanowires, the annealing temperature is higher, 550 °C, due to the higher decomposition temperature of gallium oxide (Hjort et al., 2013).

Another method to obtain clean and well-ordered surfaces with III–V semiconductor nanowires consists of protecting the sidewalls prior to their transfer in air (Xu et al., 2012). It is quite suitable for nanowires grown with molecular-beam epitaxy, where a thin layer of As can be deposited at room temperature for 30–50 min under high As₂ flux (third scheme in Figure 10.2(a)). Figure 10.2(b) shows an example of an InAs nanowire that has been capped with a thin amorphous As layer. In a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image, the As amorphous shell appears darker than both the InAs core and the gold droplet located at the top of the InAs core. A subsequent evaporation of the capping layer is usually achieved in the temperature range 350–400 °C for a few hours, monitoring the As desorption with real-time mass spectroscopy measurements, as shown in

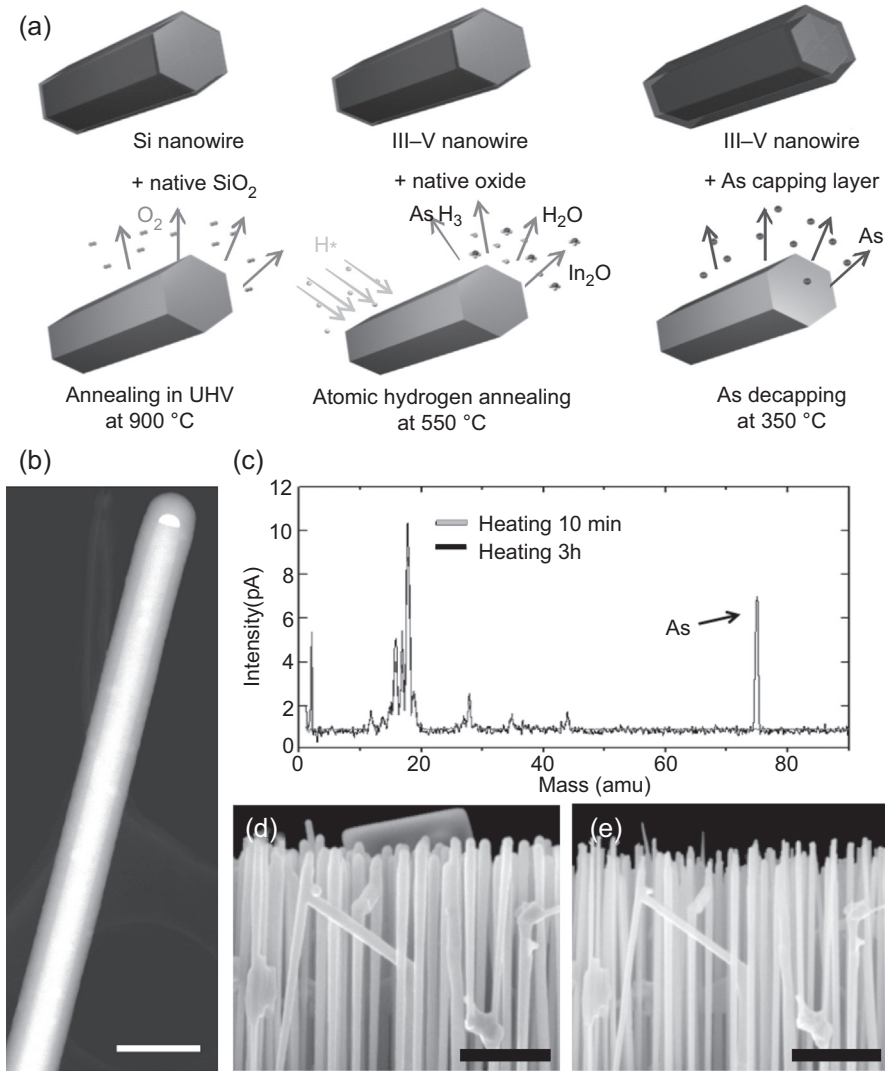


Figure 10.2 (a) Different surface treatments for the study of semiconductor nanowires with STM. (b) HAADF-STEM image of an As-capped InAs nanowire grown by molecular beam epitaxy. (c) Real-time mass spectrometry monitoring of As desorption during annealing in the STM preparation chamber at about 350 °C, under ultra-high vacuum conditions. (d, e) SEM image, in cross-section mode, of As-capped InAs nanowires before and after the desorption of the capping layer. The scale bar is 200 nm in (b), 1 μm in (d) and (e).

Figure 10.2(c). **Figure 10.2(d) and (e)** compare the same sample of vertically aligned InAs nanowires grown on an InP substrate before and after the evaporation of the As capping layer. The scanning electron microscopy (SEM) image obtained after the removal of the protecting layer clearly shows thinner nanowires, while no significant

modification of the overall morphology is observed. In addition, the low evaporation temperature of the amorphous As layer ensures that the nanowires keep their structural and chemical properties unchanged with respect to the as-grown nanowires. This method has been applied not only to InAs nanowires, but also to GaAs nanowires and ternary compounds such as InAsSb nanowires (Capiod et al., 2013; Durand et al., 2013; Xu et al., 2012).

Whatever the method used to obtain clean nanowire sidewalls, the nanowires have to be subsequently transferred onto another conducting substrate, which has also been prepared in UHV. This can be done by manipulating a sample of vertically oriented nanowires into direct contact with the substrate, as described in Figure 10.3(a). By carefully rubbing the samples, the majority of the nanowires is cleaved close to their base and usually falls flat on the surface. In the example shown in Figure 10.3(b) for $\langle 111 \rangle$ -oriented Si nanowires, the nanowires were not all vertically oriented during the growth. But keeping the manipulation along a given direction usually results in a good parallel alignment of the nanowires, with a spacing that is appropriate to easily locate a single nanowire (see Figure 10.3(c)).

Finally, in order to get a physical insight into the nanowire bulk properties such as the nature and concentration of the bulk impurities, or the interface roughness of core-shell nanowires, the nanowires can be cleaved to exhibit a cross-section through

(a) Nanowire transfer in UHV

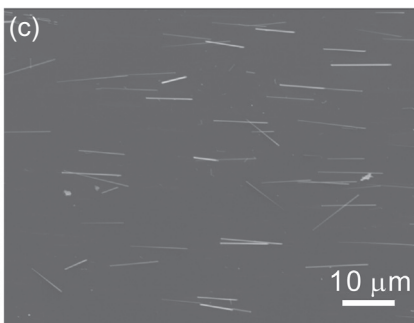
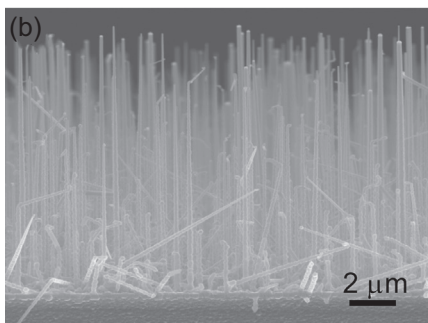
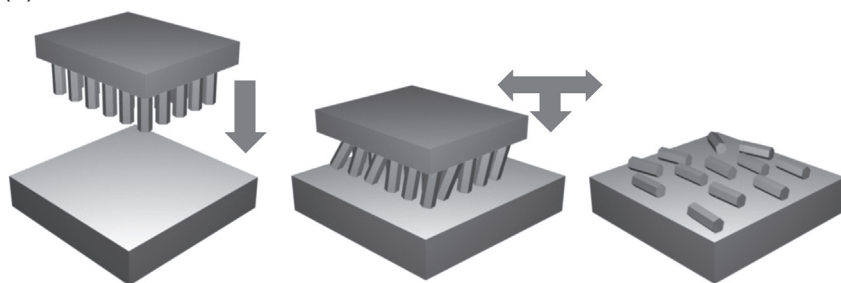


Figure 10.3 (a) Nanowire transfer procedure in UHV. (b) SEM image of $\langle 111 \rangle$ -oriented Si nanowires grown by chemical vapor deposition before the manipulation of the sample. (c) SEM image of Si nanowires deposited on a fresh Si (111) 7×7 surface.

their volume. Such a technique requires the embedding of the nanowires in a lattice-matched matrix to avoid strain and produce atomically flat surfaces. The matrix, which has a different chemical composition, also gives a significant contrast in the STM image with respect to the nanowire material. It is suitable for III–V materials, since they are known to easily cleave and expose a {110} plane, when the samples are thin enough (substrate thickness <150 nm) (Salemink, Johnson, & Albrektsen, 1994). It can also be accomplished with group IV materials that generally expose a (110) or a (111) plane. However, for spectroscopic studies of the electronic structure, it requires the production of unpinned surfaces. This can be achieved with III–V compounds, since the {110} crystallographic plane has the convenient property to have dangling bond energies outside the bulk band gap, enabling the resolution of bulk-like features in the spectroscopic measurements. In contrast, Si surfaces are dominated by dangling bond surface states and perfect passivation may be difficult to attain. As a result, cross-sectional STM imaging has been successfully applied to GaAs nanowires, when the wires were subsequently covered with an AlGaAs layer (Ouattara et al., 2007). We note that positioning the STM tip over the region of interest on the cleaved samples can be a nontrivial matter. Generally, the sample edge is used as a reference to locate the epitaxial layer that contains the nanowires. But depending on the nanowire orientation and density, the location of a nanowire can be time-consuming.

10.2.4 Related techniques

During STM operation, a variety of forces between the tip and the nanowire surface are involved depending on the separation between both electrodes. Unlike the tunneling current, which has a very strong distance dependence, the forces can be classified as short-range forces such as chemical forces, or long-range forces including Van der Waals interactions, electrostatic and magnetic forces, and adhesion forces, in particular in air when a meniscus is formed between the tip and the nanowire. When these forces are exploited instead of the tunneling current, the technique is called scanning force microscopy or atomic force microscopy (AFM). It relies on the detection of forces between the tip and the sample through the measurement of the deflection of a cantilever beam that has the tip mounted at its end.

In the static mode of operation, the force directly translates into a deflection. It requires the deflection of the cantilever to be significantly larger than the deformation of the tip and the sample. Since the force interaction does not depend on electrically conducting samples, AFM can be applied to study low-conducting semiconductor nanowires or even nanowires with insulating sidewalls. It is quite convenient to manipulate nanowires on a surface and investigate their mechanical deformation (Conache et al., 2008). But the technique can also be used with a conducting tip to probe the electronic or dielectric properties of a nanowire, and it is then named conducting AFM (C-AFM) or scanning capacitance microscopy (SCM) (Bleszynski et al., 2007; Borowik et al., 2012; Wu, Xiang, Yang, Lu, & Lieber, 2004).

Another mode exists, where the cantilever deliberately vibrates, with either a change in amplitude (amplitude modulation) or a change in frequency (frequency modulation). These operation modes have led to AFM-related techniques, such as

electrostatic force microscopy (EFM), scanning surface potential or Kelvin force microscopy (KFM), and scanning photocurrent microscopy (SPCM). They are generally used to investigate the doping distribution and the transport properties in semiconductor nanowires, through the analysis of the spatial variation of the photoconductivity (Dan et al., 2011; Gu, Romankiewicz, David, Lensch, & Lauhon, 2006; Koren, Berkovitch, & Rosenwaks, 2010; Koren, Rosenwaks, Allen, Hemesath, & Lauhon, 2009; Yang, Li, Wu, Oh, & Yu, 2012).

10.3 Exploring the surfaces of semiconductor nanowires at the nanoscale

10.3.1 Understanding the growth dynamics from the surface

The growth of a semiconductor nanowire promoted by a metal seed particle usually proceeds through the vapor–liquid–solid (VLS) mechanism in which reactants from the vapor phase form a supersaturated liquid alloy inside the particle, and then crystallize at the liquid–solid interface under the seed particle. In the simplest growth models, the reactants are directly trapped by the seed particle from the gas phase. But reactants can also adsorb on the nanowire sidewalls, and if surface diffusion occurs, they can reach the seed particle to contribute to the growth. For example, the diffusion length of Ga adatoms on a clean and ordered GaAs(111) surface has been found to be around 1 μm (Koshiba et al., 1994). This diffusion length is large enough to allow the adatoms to diffuse from the base of a nanowire and reach the nanowire tip (Dubrovskii et al., 2009). Depending on the growth conditions, the kinetic processes on the sidewalls can be quite complex involving diffusion toward the seed particle but also away from the seed particle (Dubrovskii et al., 2012). In addition to the diffusion of precursors, the metal atoms might diffuse from the seed particle onto the nanowire sidewalls (Cao et al., 2006; Hannon, Kodambaka, Ross, & Tromp, 2006; Kawashima et al., 2008). Yet, metal adsorption on semiconductor surfaces maintained at elevated temperatures are known to induce significant changes going from the modification of the surface atomic reconstruction up to a strong faceting of the surface (Seehofer, Huhs, Falkenberg, & Johnson, 1995; Yagi, Minoda, & Degawa, 2001).

In order to understand and control the structural changes induced by metallic atoms on the morphology of semiconductor nanowires, it is very useful to combine different analysis techniques. Here, $\langle 111 \rangle$ -oriented Si nanowires were grown at low silane partial pressure by Au-catalyzed chemical vapor deposition (flow rate of SiH_4 and Ar of 12 and 150 standard cubic centimeters per minute, total pressure of 1.1 mbar, growth temperature of 550 $^\circ\text{C}$). From SEM observations (Figure 10.4(a)), the Si nanowires consist of six $\{112\}$ sidewalls, with alternating large and narrow widths. The sidewalls show facets that are better resolved in the high-resolution TEM image (Figure 10.4(b)), where two downward facets surround an upward $\{111\}$ facet. The largest one corresponds to a $\{113\}$ plane, whereas the smallest one is measured to be about 38.9° off a $\{111\}$ plane, indicating that it is a $\{115\}$ facet. The HAADF-STEM image (Figure 10.4(c)) shows that the facets are periodically covered

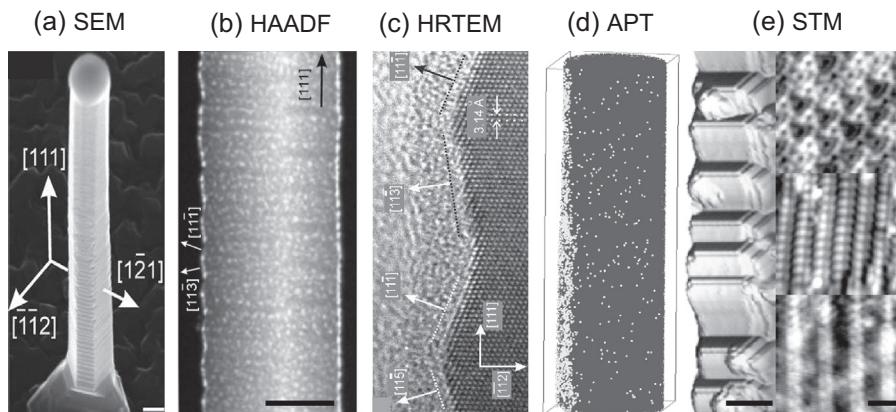


Figure 10.4 (a) SEM image of a $[111]$ -oriented Si nanowire grown on a Si(111) surface from a gold seed particle. The orientations of two sidewalls are indicated. Scale bar: 50 nm. (b) HAADF-STEM image of an Si nanowire, where Au clusters appear as bright protrusions decorating the nanowire sidewalls. Scale bar: 20 nm. (c) High-resolution TEM image of a 75-nm-diameter Si nanowire. (d) Three-dimensional atom probe tomography atom-by-atom map of a portion of a $\langle 111 \rangle$ -oriented Si nanowire included a nanowire sidewall. Si and Au atoms correspond to dark and bright dots, respectively. The volume of the analyzed portion is $30 \times 27 \times 143 \text{ nm}^3$. (e) Left: three-dimensional STM image of a Si nanowire sidewall. Scale bar: 20 nm. Feedback parameters: 1.6 V, 100 pA. Right: STM images of (top) a Si(111) facet, (middle) a Si(115) facet, and (bottom) a Si(119) facet. Feedback parameters: (top) 1.3 V, 100 pA; (middle) 2.0 V, 500 pA; (bottom) 2.0 V, 500 pA. Scale bar: 2 nm. All STM images were obtained at 77 K.

with numerous bright protrusions. The HAADF, or so-called Z contrast, imaging strongly depends on the sensitivity of the technique to the atomic number (Z). This means that the heaviest atoms appear brighter in the image, suggesting the formation of small Au-rich clusters on the high-index planes due to the diffusion of Au from the seed particle. The chemical composition of these clusters is confirmed by atom probe tomography (APT) that can map the three-dimensional distribution of atoms at the atomic scale. It indicates that Au atoms are mainly detected at the surface of the nanowire, as shown in the reconstructed volume of [Figure 10.4\(d\)](#).

In order to obtain the atomic structure of the different facets, STM experiments were also performed, following the preparation procedure described in [Section 10.2.3](#). The large-scale STM image in [Figure 10.4\(e\)](#) is a three-dimensional STM view of an Si nanowire sidewall, where facets are found to alternate between $\{111\}$ planes and high-index planes with $\langle 113 \rangle$, $\langle 115 \rangle$, and $\langle 119 \rangle$ orientations, which were deduced from the angle between the normal vector of the facet and the $[\bar{1}\bar{1}1]$ growth direction with an uncertainty of $\pm 1^\circ$ ([Xu et al., 2010](#)). The STM reveals the existence of Au-rich clusters on the wider high-index planes consistent with the results provided by the other analysis techniques. In addition, the atomically resolved STM images indicate the existence of atomic reconstructions that differ from the well-known reconstructions usually observed for the same crystallographic planes ([Baski,](#)

Erwin, & Whitman, 1997). For example, the (111) facet in the upper and right STM image of Figure 10.4(e) does not show the well-known 7×7 reconstruction. Instead, a hexagonal lattice with a sixfold periodicity with respect to the Si(111) substrate is observed. Such a structure is similar to the one found by Nogami, Baski, and Quate (1990) and Yamazaki, Matsuda, Okino, Morikawa, and Hasegawa (2005) after the adsorption of gold on the Si(111) surface, and corresponds to the 6×6 phase of the Au/Si(111) surface (Xu et al., 2010). Since the 6×6 phase on the Au/Si(111) surface occurs for Au coverage higher than 0.96 monolayer (Nagao et al., 1998), the Au coverage on the sidewalls is estimated to be around 1 monolayer (equivalent to 7.84×10^{14} Au atoms/cm²). As to the high-index facets, they consist of stripes. The stripes are well resolved for the {115} facet (mid-right image of Figure 10.4(e)) and correspond to atomic rows yielding a 4×2 structure. In contrast, the stripes of the {119} facets (bottom right image of Figure 10.4(e)) are more complicated to interpret, but periodic structures are still visible.

Therefore, the observed atomic structure of the facets indicates that gold completely wets the sidewalls of the Si nanowires and certainly contributes to the sawtooth morphology of the sidewalls. Indeed, even when a facet is far away from the seed particle, the gold activity is maintained, and depending on the Au coverage, gold can stabilize the facets with different orientations (Wiethoff, Ross, Copel, Horn-von Hoegen, & Meyer zu Heringdorf, 2008). Replacing Au by Al as the catalyst material has revealed the formation of atomically smooth sidewalls, in sharp contrast with the sawtooth facets of the Si nanowires grown with a gold seed particle. This effect is attributed to the Al-induced stabilization of the {112} sidewalls, as indicated by SPA-LEED and STM characterization of the Si(112) surfaces (Moutanabbir et al., 2011), making STM experiments quite attractive to understand the overall morphology of the sidewalls as a function of their coverage with catalyst materials.

10.3.2 Surface reconstruction and electronic properties

Crystal-phase engineering in nanowires, which means controlling polytypism stacking faults and twin defects along the nanowire growth, presents unique opportunities to observe novel fundamental properties (Akiyama, Yamashita, Nakamura, & Ito, 2010; Ikonc, Srivastava, & Inkson, 1993; Tsuzuki et al., 2011; Zhang et al., 2010). These structural modifications of the bulk crystal usually occur along with a change of the surface orientations (Bauer, Gottschalch, & Wagner, 2008; Lugani et al., 2011). Therefore, understanding surface structure and surface composition is of particular importance for nanowire applications, since they might strongly contribute to the electrical, optical, and thermal properties of the nanowires (Moore, Saha, Prasher, & Shi, 2008; Sködl et al., 2005; Thelander et al., 2010). A prototypical material is GaAs, where polytype inclusions consisting of zinc-blende (ZB) and wurtzite (WZ) segments form during the growth of nanowires. Typical GaAs nanowires grown by molecular epitaxy have a hexagonal shape with six sidewalls (see the schematic top view of Figure 10.5(a)). As described in Figure 10.3, STM images of a nanowire are obtained by cleaving the nanowires onto another conducting substrate. Then, for

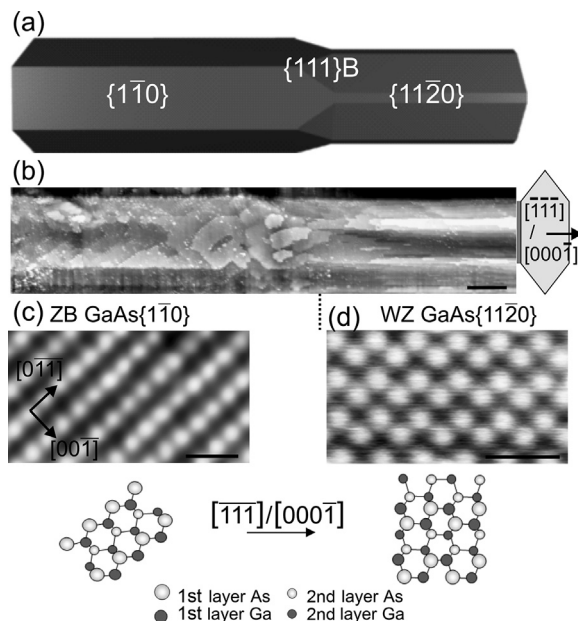


Figure 10.5 (a) Three-dimensional model of a ZB/WZ interface in III–V nanowires grown along the equivalent $[\bar{1}\bar{1}\bar{1}]/[000\bar{1}]$ directions. (b) Large-scale STM image of a sidewall acquired on a GaAs nanowire segment that exhibits a ZB structure to the left and a WZ structure to the right. Scale bar: 25 nm. (c, d) High-resolution STM images of the GaAs ZB and WZ phases measured at 20 and 100 pA, and -3.5 and $+2.0$ V, respectively. Scale bar: 1 nm. The corresponding atomic surface structures are shown below.

nanowires with a constant diameter along the axial direction, one of the sidewalls is in contact with the substrate and the opposite one parallel to the scanning plane. In this way, the morphology of a sidewall can be imaged, as shown in [Figure 10.5\(b\)](#).

The sidewall edges are imaged as two lines running parallel to the growth direction, where the contrast changes from bright to dark as the tip scans over the adjacent and tilted sidewalls. This change is less pronounced at the bottom of the STM image due an asymmetric shape of the tip. Focusing on the top (parallel to the substrate) sidewall, we note a clear difference in the morphology of the terraces between the left and right parts of the image. To the left, the flat terraces are defined by step edges along two preferential directions, the $\langle 011 \rangle$ and $\langle 001 \rangle$ directions, consistent with ZB structure GaAs $\{110\}$ planes. This crystallographic orientation is confirmed with a high-resolution STM image ([Figure 10.5\(c\)](#)), which shows the anion sublattice consisting of parallel atomic rows, making an angle of 35.3° with the $\langle 111 \rangle$ B growth axis. Indeed, for this plane, the atomic relaxation involves a bond rotation that results in a buckling of the surface atoms. These atomic displacements lead to a charge transfer from the dangling bond localized on the cations to the dangling bond localized on the anions. It pushes the surface states associated with the broken bonds out of the bulk band gap: the dangling bond localized on the anions becomes occupied, whereas

the dangling bond localized on the cations becomes empty. Therefore, only the occupied surface states associated with As atoms are imaged at negative sample bias, and the linear rows consisting of periodic bright protrusions seen in the STM image of Figure 10.5(c) are consistent with the atomic lattice indicated below the image. Switching the voltage polarity gives access to both types of atoms, and the precise registry of the As and Ga atoms can usually be achieved by recording simultaneously forward and backward scan lines at alternate biases (Feenstra, Stroscio, & Fein, 1987).

In the right part of Figure 10.5(b), the terraces are horizontally elongated and much narrower, with the step edges propagating along the growth direction. Such a morphology is typical of the facets observed on cleaved WZ crystals (Siemens, Domke, Ebert, & Urban, 1999). Imaging the terraces at high resolution reveals the existence of zigzag rows, a signature of WZ structure GaAs(11 $\bar{2}$ 0) sidewalls, which are known to be the counterpart of the ZB {110} facets for nanowires with a growth axis along the equivalent $[\bar{1}\bar{1}\bar{1}]/[000\bar{1}]$ directions (Eisele & Ebert, 2012). Again the observation of one type of atom is explained by the voltage-dependence of the STM images, where the cation sublattice is imaged this time. Similar results have also been obtained with WZ InAs nanowires, not only for the (11 $\bar{2}$ 0) sidewalls but also for the (10 $\bar{1}$ 0) sidewalls (Hilner et al., 2008).

By exploiting the chemical contrast mechanism valid for most of the III–V semiconductor (110) surfaces using different tunneling biases, STM has the ability to identify impurities and other III or V elements in ternary or quaternary compounds. For example, Figure 10.6 shows an InAs/InAs_{1–x}Sb_x heterostructure nanowire grown by molecular-beam epitaxy. In the large-scale STM image (Figure 10.6(a)), the gold seed particle is clearly seen at the top of the nanowire (left part of the image), while a small constriction, indicated by the dotted line, appears 1 μm below this particle. We attribute the constriction to the interface between the top InAs_{1–x}Sb_x segment and the bottom segment. The interface is better seen in the enlarged view of Figure 10.6(b), and corresponds to the point along the growth axis where a strong structural change with respect to the sidewall roughness occurs. The left InAs_{1–x}Sb_x segment reveals a top sidewall that is flat and bordered by two sawtooth-faceted sidewalls. On this flat sidewall, the atomic structure looks similar to the one observed for the GaAs (110) sidewalls in Figure 10.5(c). It consists of parallel atomic rows running along a $\langle 110 \rangle$ direction, making an angle of 35.3° with the $[\bar{1}\bar{1}\bar{1}]$ -B growth axis. Therefore, we attribute this sidewall to a {110} plane of a ZB crystal. We note the existence of twin boundaries perpendicular to the growth direction that lead to a rotation of the crystallite by 60° around the growth axis. Such rotations explain why the edges of the {110} sidewalls exhibit a sawtooth shape: as the twins are formed through the whole cross-section of the nanowire, trenches build up in antiphase and account for the roughness of the adjacent sidewalls. This roughness was rarely observed by SEM inspections, because of its small dimensions, illustrating the need for complementary local probe techniques and electron microscopy. Remarkably, numerous bright protrusions with an atomic size are seen, when the anion sublattice is imaged. Based on previous cross-sectional STM studies of antimonide-based alloys (Steinshneider et al., 2000; Timm et al., 2008), we identify the bright protrusions to Sb atoms, due to the

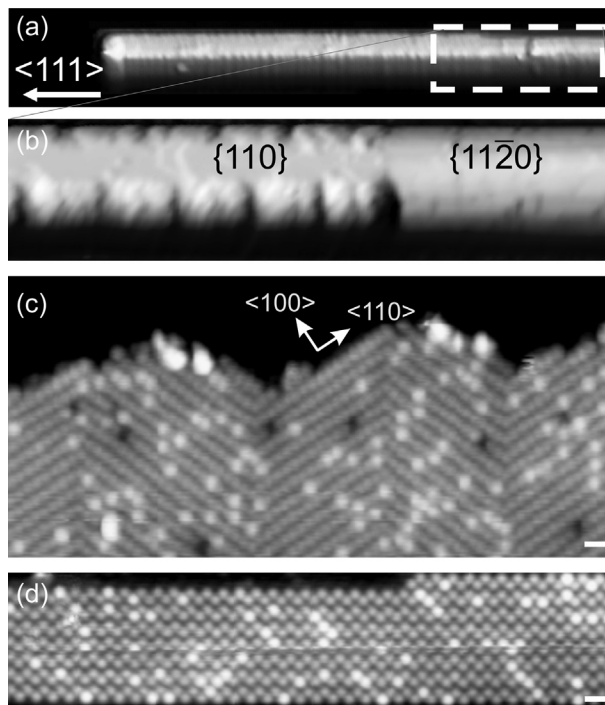


Figure 10.6 (a) Large-scale three-dimensional STM image of a $[000\bar{1}]/[\bar{1}\bar{1}\bar{1}]$ B-oriented InAs/InAs $_{1-x}$ Sb $_x$ nanowire lying flat on a Si(111) surface. The nanowire mean diameter is 85 nm. (b) Close-up view of the interface region between the InAs and InAs $_{1-x}$ Sb $_x$ segments. (c) High-resolution STM image of a $\{110\}$ sidewall on the InAs $_{1-x}$ Sb $_x$ segment. (d) High-resolution STM image of a $\{11\bar{2}0\}$ sidewall on the InAs segment. The STM images were acquired with a tunneling current of 10 pA and sample voltages between -3.0 and -3.5 V. Scale bar: 1 nm.

higher energy of the Sb-related surface state. The statistical analysis yields a fraction of bright atoms with respect to the total number of anions of 14%.

For sufficiently high Sb concentrations, the composition determined by STM can be compared with the one obtained by X-ray energy-dispersive spectroscopy (XEDS) point analysis performed just below the seed particle (typically about 50 nm from the nanowire–particle interface), where virtually no overgrowth is present, and on the sides of the InAs $_{1-x}$ Sb $_x$ segment. The XEDS analysis revealed a Sb composition of 12–13% of Sb on the sides of this segment, consistent with the concentration deduced from STM. Interestingly, XEDS analyses in the middle of the segment or just below the seed particle indicated a smaller Sb concentration, indicating that a thin shell with a higher Sb concentration covers the nanowire core. The existence of this shell is confirmed when a $\{11\bar{2}0\}$ sidewall of the bottom segment is imaged at the atomic scale (Figure 10.6(d)). Bright protrusions corresponding to Sb atoms are again visible, although the segment was expected to consist of pure InAs. Therefore STM can provide detailed information on the chemical composition at the surface of nanowires that is hardly achieved with other characterization techniques.

Similar variation of the contrast can be obtained with misplaced atoms or foreign atoms. Their presence modifies the periodic potential of the perfect crystal, and depending on the strength of the perturbation, the defect can either introduce new energy levels in the forbidden gap of the semiconductor materials or scatter the electrons, when their energy lies within the allowed energy bands of the crystal, resulting in a change of the density of states. Since in STM the tunneling current depends on the density of states, the presence of a point defect at the surface or a few layers below the surface should result in the deflection of the tip when the tip moves above the defect, enabling the direct observation of single-point defects, as shown in cleaved GaAs nanowires for example (Mikkelsen, Sköld, Ouattara, & Lundgren, 2006).

Moreover, as the tunneling current contains information about the electronic structure of the surface, measuring tunneling spectra makes it possible to qualitatively determine the electronic properties of the nanowire sidewalls. The spectra can even provide the nanowire crystal bandgap, when the surface states are not localized in the material bandgap or their density is quite small in comparison to the bulk states. Figure 10.7 shows typical tunneling spectra measured on (110) sidewalls of a GaAs nanowire and a $\text{GaAs}_{1-x}\text{Sb}_x$ nanowire at 77 K. On these surfaces, the dangling bond surface states are resonant with the conduction and valence bands, and thus the bulk bands are predominantly observed. The valence band is seen at negative voltages and the conduction band at positive voltages. Both bands are separated by an apparent bandgap defined as the region where the tunneling current reaches the experimental noise level (indicated by E_V and E_C in Figure 10.7). The one with the larger width of about 1.5 eV is consistent with the bulk bandgap of GaAs (Brammertz et al., 2006), whereas the smaller apparent gap measures 0.8 eV, slightly smaller than the bandgap expected for an intended concentration of 50% of Sb at 77 K.

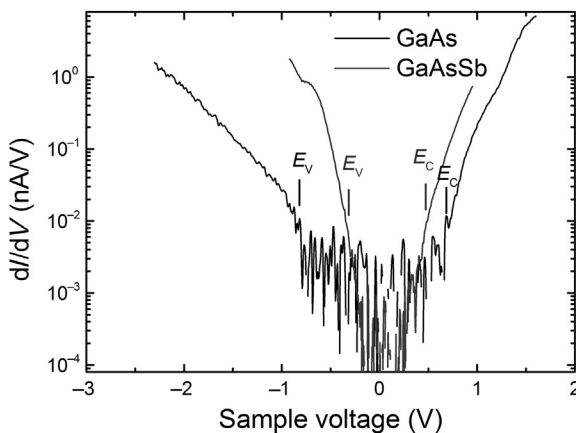


Figure 10.7 Tunneling spectra acquired at the surface of ZB GaAs and $\text{GaAs}_{0.5}\text{Sb}_{0.5}$ nanowires at a temperature of 77 K. The valence band maximum (E_V) and the conduction band minimum (E_C) are indicated by vertical segments.

For undoped (or low-doped) GaAs with no intrinsic surface states in the bandgap and *no pinning* of the Fermi level at the surface, tunneling spectra usually exhibit very large apparent bandgaps (voltage region with no tunnel current), due to the large tip-induced band-bending that is not damped by screening carriers (Jäger, Ebert, Urban, Krause-Rehberg, & Weber, 2002). As a result, for semi-insulating GaAs(110) with residual *n* (*p*)-type carriers, the branch at positive (negative) voltages in the tunneling spectra does not exist (below noise threshold) (Jäger et al., 2002) or is significantly shifted to much larger voltages. This effect is visibly not observed here. Instead we clearly observe both bands in the tunneling current curve. This indicates that the Fermi level is pinned at ZB surfaces. Since the intrinsic surface states of the ZB (110) surfaces are outside of the bandgap, the pinning of the Fermi level must arise from an extrinsic source, such as defects. We attribute the Fermi level pinning to the numerous step edges visible on the nanowire sidewalls, as shown in Figure 10.5(b). Steps on the GaAs(110) surface induce defect states in the bandgap, which—when present at a sufficiently large concentration—induce a pinning of the Fermi energy in midgap position (Gaan et al., 2012; Sabitova et al., 2013). For the GaAs nanowire investigated here, the steps have a concentration of $10^5/\text{cm}$ on the ZB segment. This number corresponds to a defect state concentration of $4 \times 10^{13}/\text{cm}^2$, assuming one defect state every lattice unit along the step edge. Such a high concentration is enough to induce a complete pinning of the Fermi level. This pinning is expected to be rather general, since the sidewalls of nanowires usually consist of atomic terraces or facets. Therefore, it has to be taken into account for charge transport measurements in nanowires with small diameters, because it strongly affects the band bending at the surface.

10.4 Studying transport in semiconductor nanowires

10.4.1 Single-tip experiments

Integration of semiconductor materials onto silicon has so far failed in thin-film technology, due to interfacial lattice mismatch that can propagate through the entire crystal. This obstacle can be overcome with nanowires, because the mismatch can be relaxed at the nanowire edge for small-diameter nanowires. As a result, the integration of III–V and II–VI semiconductor materials with the highly mature Si technology has been demonstrated (Mårtensson et al., 2004; Ng, Yamada, Nguyen, Chen, & Meyappan, 2004; Russo-Averchi et al., 2012; Tang et al., 2008; Tomioka, Yoshimura, & Fukui, 2012; Uccelli et al., 2011). Crucial parameters for the electrical and optical performances of nanowire devices are the bandgap, carrier concentration, and carrier mobility. While the knowledge of these parameters is usually achieved for nanowires that have been separated from the substrate on which they have been grown, the electrical transport properties of epitaxial nanowires, which are still connected to their substrate, are critical for device design and direct comparison with the existing thin-film technologies. Therefore, contacting a nanowire with a single probe is a suitable technique to determine its electrical properties. Since nanowire growth usually relies on the

so-called VLS mechanism, which involves the use of a metal seed particle, the formation of a good contact can be achieved by positioning the probe in direct contact with the seed particle.

An illustration of this characterization method is given for Ge nanowires grown on a Si(111) substrate in Figure 10.8 (Dubrovskii et al., 2012; Kramer et al., 2009; Xu et al., 2011). In this case, the epitaxial growth of Ge nanowires assisted by Au seed particles leads to two different orientations: the shortest ones appear normal to the surface and grow along the [111] direction, whereas the longest ones point at 54.7° from the

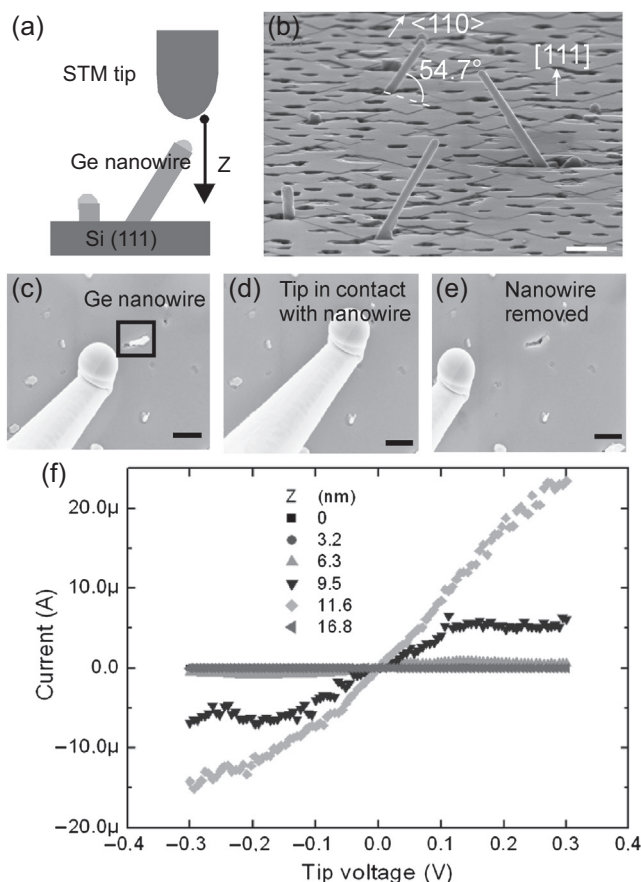


Figure 10.8 (a) Schematic diagram for contacting a nanowire with an STM tip. (b) SEM image of Ge nanowires grown on a Si(111) surface by molecular beam epitaxy. The orientations of the nanowires are indicated in the image. Scale bar: 400 nm. (c)–(e) Sequence of SEM images obtained before contacting a $\langle 110 \rangle$ -oriented Ge nanowire, during the acquisition of the transport measurements shown in (f) and after the cleavage of the nanowire. (f) I – V curves measured on a Ge nanowire for different tip displacements Z toward the substrate.

surface plane, as shown in Figure 10.8. These inclined Ge nanowires, which can reach a length of 2 μm above the overgrown Ge layer, are found to grow along three different directions only. When projected in the (111) surface plane, the directions make an angle of 60° , corresponding to equivalent $\langle 110 \rangle$ directions. In the top view of a scanning electron micrograph, such as the one shown in Figure 10.8(c), the $\langle 110 \rangle$ -oriented Ge nanowires are thus recognizable. If the scanning electron microscope contains a probe that is controlled by piezo-motors with coarse and fine motion control, then the nanowire can be connected with the probe. Because the nanowires are tilted, the use of a blunt STM tip ensures that the electrical contact will occur with the Au seed particle, since it is the most protruding part of the nanowire.

The electrical characteristic in Figure 10.8(f) reveals a rather symmetric variation of the current as a function of the voltage between negative and positive polarities, when the tip is in contact with minimal stress. An ohmic behavior is found at small bias. By increasing the mechanical strain, the current intensity increases and the characteristic becomes asymmetric, up to the point where the tip approach is larger than 3.1 nm. Then the current intensity decreases and even reaches zero, indicating the breaking of the nanowire, as shown by the loss of the nanowire from the substrate in the scanning electron micrograph of Figure 10.8(e). So far, most of the similar experiments performed with group-IV semiconductor nanowires have shown the importance of the surface defects to account for the conductivity of the nanowires (Bauer et al., 2007; Léonard, Talin, Swartzentruber, & Picraux, 2009). In the case of the Ge nanowires described here, it was found that Au may completely diffuse away from the original seed particle, causing the formation of small Au-rich clusters on the sidewalls of the nanowires (Xu et al., 2011), which will cause a modification of the nanowire transport properties.

Similar experiments have also been performed with arrays of vertically aligned III–V semiconductor nanowires (Talin, Léonard, Swartzentruber, Wang, & Hersee, 2008; Talin, Swartzentruber, Léonard, Wang, & Hersee, 2009; Talin et al., 2010). In the absence of a SEM to position the probe on top of a single nanowire, the empty space between the nanowires can be filled with an insulating layer, for example by using a template approach where nanoscale growth windows are defined in a silica mask (Deb et al., 2005). Then, the conductive tip of a C-AFM safely scans the surface containing the protruding nanowires and can be immobilized on top of a nanowire in order to acquire I – V characteristics (Deb et al., 2006).

Scanning an array of vertically aligned nanowires can also be used to probe the mechanical deformation of nanowires. In contrast to STM, the force applied with an AFM is known and as a result the mechanical deformation of semiconductor nanowires makes it possible to study their elasticity, strength, and plasticity (Gordon, Baron, Dhalluin, Gentile, & Ferret, 2009; Tang et al., 2012). In the case of ZnO nanowires, which are piezoelectric, the mechanical deformation of a nanowire creates a strain field and a charge separation across the nanowire, followed by a discharge that generates an electric current. This approach thus makes it possible to study the conversion of mechanical energy into electric energy at the nanoscale and also to investigate the piezoelectric response of semiconductor nanowires to design piezotronic devices (Gao and Wang, 2007; Lu et al., 2009; Wang and Song, 2006).

10.4.2 Multiple-point probe measurements

In single-tip experiments, characterization of the transport is usually achieved by contacting the metal seed particle with a metallic tip. However, the growth of semiconductor nanowires can sometimes occur without any seed particle, or the integration of the nanowires might require the removal of the seed particle prior to their characterization. As a result, the measurement of nanowire electrical resistivity depends on the resistance of the probe and the contact resistance between the probe and the nanowire. The advantage of using the four-point method is that it eliminates the parasitic resistance introduced by the probe. Figure 10.9 shows SEM images of an array of InAs nanowires, where four STM tips have been brought into electrical contact with a single nanowire. The nanowires were kept on the InP substrate (seen on the left) and exposed to the air during their transfer toward the UHV system that hosts a

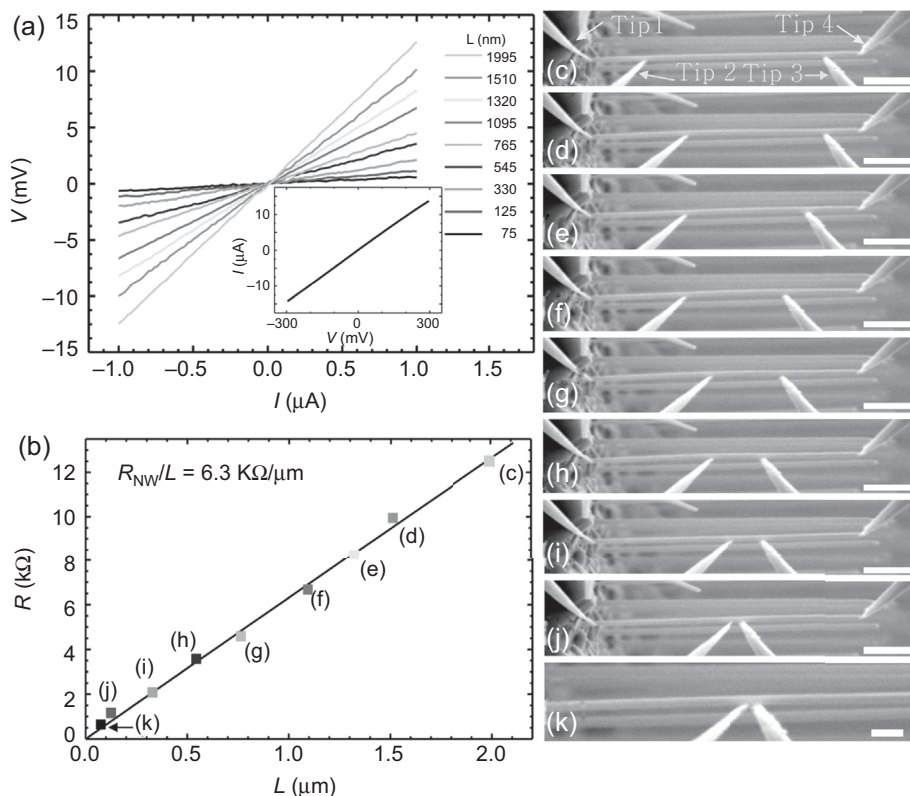


Figure 10.9 (a) $V-I$ curves measured with the four-probe method for different spacings L between tips 2 and 3. Lower inset: $I-V$ curve measured between tip 1 and the substrate. (b) Resistance measured from the $V-I$ measurements as a function of L . (c)–(k) Sequence of SEM images of free-standing InAs nanowires that were grown on an InP(111)B substrate visible at the left part of the image. The nanowire in the center is contacted by four W tips. Scale bar: 500 nm, except for the bottom SEM image: 200 nm.

SEM and a multiprobe scanning tunneling microscope. As a result, their sidewall is covered with a thin oxide layer. Thanks to the precision of the STM scanners, four tips were brought into electrical contact with the nanowire visible in the center of the SEM image. The outer tips are respectively connected to the top and the base of the wire and used as source and ground electrodes for driving the current through the wire. The inner tips are the potential probes. Because the resistance of the voltmeter is very large, the probe resistance and probe-to-nanowire contact resistance can be neglected. Thus, the measured resistance corresponds to the resistance of the nanowire only.

In most cases, the $I(V)$ curve between a single tip and the substrate, held at ground, has an ohmic behavior, as shown in the lower inset of Figure 10.9(a), where the measured resistance is 20 k Ω . We attribute this small resistance value to the oxide breakdown when the tip is brought into contact. Then, the next tips are also brought into contact with the wire and a current is passed through the wire. The related potential drop measured between the inner probes is found to be linearly proportional to the current intensity and the gradient of the curve yields the four-probe resistance of the wire for a given separation between the inner probes. By moving the inner tips toward the center of the wire, as shown by the sequence of SEM images in Figure 10.9(c), a set of $V(I)$ characteristics was acquired for different tip separations L (Figure 10.9(a)). From these $V(I)$ curves, the resistance is found to linearly increase with L (Figure 10.9(b)). The slope yields a resistance per unit length of 6.3 k $\Omega/\mu\text{m}$.

Since InAs materials are known to exhibit a surface electron accumulation layer (Olsson et al., 1996), the dependence of the nanowire resistivity on the surface chemistry was also investigated to determine whether the transport predominantly occurs in the bulk or rather in the accumulation layer below the surface. For that study, InAs nanowires were either protected with a thin layer of As, that was evaporated as described above, or passivated with an ammonium sulfide solution to produce a chemisorbed S layer on their surface. Indeed this chemical strategy has been shown to efficiently remove the native oxide on the InAs (001) surfaces, offering greater chemical stability to electronic devices (Petrovykh, Long, & Whitman, 2005). As evidenced in Figure 10.10, a change of the surface chemistry for nanowires with similar diameters causes a significant variation of their resistance per unit length. The lowest resistance is obtained for the S-passivated nanowires. This is consistent with the depth of the accumulation layers measured for InAs surfaces prepared with different chemical treatments (Petrovykh, Yang, & Whitman, 2003). Surprisingly, the nanowires that were prepared by evaporating the As capping layer in UHV, so that the initial crystalline surface structure of the nanowires could be restored, show the highest resistance. In order to understand the physical origin of this resistivity increase, the surfaces of the nanowires were subsequently imaged with STM. While the upper inset of Figure 10.10 shows a large-scale STM image of an InAs nanowire, with the Au seed particle seen at the NW top (left), the high-resolution STM image reveals the existence of atomic rows running perpendicular to the growth axis. This atomic structure is consistent with the atomic rows that form on a $\{10\bar{1}0\}$ wurtzite sidewall (Ebert, 1999; Feenstra, Stroscio, & Fein, 1987). Interestingly, small clusters are also visible and are generally observed close to the edge of the sidewalls. The formation of Au

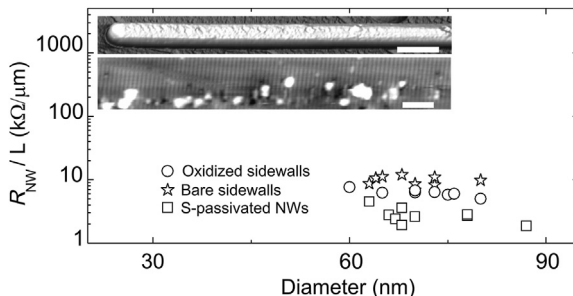


Figure 10.10 Resistance per unit length $R_{NW/L}$ of InAs nanowires measured for different diameters and surface treatments. Inset (top): Large-scale STM image of a cleaved InAs nanowire deposited on a Si(111) surface. Inset (bottom): High-resolution STM image of a $\{10\bar{1}0\}$ sidewall. The STM images were obtained at a sample voltage and tunneling current of (top) -0.47 V, 3 nA and (bottom) -3.00 V, 20 pA. Scale bars are 150 and 4 nm, respectively.

clusters is attributed to the diffusion of Au from the seed particle, during the evaporation of the As capping layer, because HAADF-STEM images did not show the presence of such clusters on the InAs nanowires with oxidized or passivated sidewalls. These clusters increase the electron scattering at the surface and certainly account for a lower mobility of the free carriers and thus an increase of the nanowire resistivity.

Similar experiments have been performed with other semiconductor nanowires (Korte et al., 2013; Li et al., 2012; Lin et al., 2006). For nonintentionally doped nanowires, they have revealed the importance of the surface defects in the transport properties of the nanowires. Very often, these experiments require the use of a SEM to locate a nanowire and monitor the position of the contacts with the probes. As the excitation of materials with incident electrons can generate charged defects at the surface of semiconductor materials (Han, Nakayama, & Weaver, 1999; Nakayama and Weaver, 1999), the defects change the pinning of the Fermi level at the surface. Hence the surface band bending is altered, which modifies the transport properties of the nanowire when it predominantly occurs close to the surface (Durand et al., 2013).

10.5 Conclusion

This review has been mainly focused on STM studies. The series of STM experiments reviewed in this chapter have also all been restricted to the UHV environment. However, a scanning tunneling microscope can operate in other environments such as liquids or high-pressure atmospheres. In these environments, the surface chemistry of semiconductor nanowires can be controlled, and their chemical modification investigated *in situ*. In addition, more and more setups are now able to work under high magnetic fields, and magnetic tips are currently available that should offer new prospects in the study of diluted magnetic semiconductor nanowires for spintronics. Finally, for practical industrial use, there is a strong need for profiling capability with atomic-scale resolution and time efficiency, so that the dynamics of

semiconductor electronic structure can be studied not only in real space at the nano-scale but also in real time under operating conditions. However, it has to be kept in mind that STM is a local probe technique, and as a result proximity effects inevitably affect the measurements. Although it is a powerful technique to observe, measure, and manipulate semiconductor materials, the correct interpretation of the underlying physical mechanisms is not straightforward and requires a careful analysis of the data.

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Using atom probe tomography in the study of semiconductor nanowires

11

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11.1 Introduction

Among the multiple state-of-the-art characterization techniques for nanoscale materials, atom probe tomography (APT) which is a three-dimensional analytical high resolution microscope, plays a unique and important role (Chen et al., 2012; Perea et al., 2009; Seidman, 2007). One of the advantages of APT is that a combination of high spatial resolution (depth <0.1 nm and lateral <0.3 nm) and high quantitative concentration levels (<100 ppm) with isotopes distinguishable can be obtained at the same time compared to other techniques (Moutanabbir, Isheim, Seidman, Kawamura, & Itoh, 2011). The atomic resolution of APT makes it an instrument of choice to understand and control effectively the doping process in semiconductor NWs, which is a very important aspect for their technological applications. This chapter first presents the instrumentation of APT. This technique originated with the invention of the field ion microscope (Müller, 1951) and atom probe (1968) by E. Müller (Müller, Panitz, & McLane, 1968). The laser-assisted working mode of APT is described briefly. Our introduction of the basic principles of APT gives a general view of how the assembly of atoms in semiconductor NWs is collected, interpreted, and reconstructed. The main difficulty for the analysis of an NW using the APT technique is related to the sample preparation. Different types of sample preparation methods for NW characterization by APT were developed and are also described in this chapter. Here, we have chosen Silicon NWs (SiNWs) as the typical semiconductor NWs to describe the capacities of APT.

11.2 Instrumentation

APT is a three-dimensional analytical high resolution microscope. Its principle is based on the evaporation by field effect of surface atoms from a sample in the shape of a very sharp tip. The first model of atom probe measured the chemical composition of a sample (Müller, 1951). For such analysis, the sample has to be prepared as a very sharp tip with an end radius of curvature less than 50 nm. It is then placed in ultrahigh vacuum (UHV), cooled down to 80 K, and positively polarized with a high electric

potential (V) of several kV. It results in the appearance of a high electric field (E) at the apex of the tip whose intensity is inversely proportional to the radius of curvature R of the tip (tip effect) (Eqn (11.1)).

$$E = \frac{V}{\beta R} \quad (11.1)$$

where β is a numerical factor due to the cone angle of the tip ($\beta \sim 2-8$), V is the voltage applied to the tip, and R is its radius. The small value of R (≈ 50 nm) allows E to reach a high electric field intensity of several tens V/nm, which causes the ionization and evaporation of surface atoms of the sample (NWs). The evaporated atoms are then accelerated and collected by an ion detector, which is placed in the front of the tip. The chemical nature of each evaporated atom is then accessible with mass spectrometry where the ion mass-to-charge ratio is determined via a time measurement (time of flight (ToF) mass spectrometry). By evaporating the sample atom by atom and atomic layer by atomic layer, the chemical composition at different depths of the sample can be obtained. The tomographic aspect of atom probe was developed in the early 1990s (Blavette, Bostel, Sarrau, Deconihout, & Menand, 1993; Cerezo, Godfrey, & Smith, 1988). The ion detector initially constituting the mass spectrometer has been replaced by a position sensitive detector (PSD). This type of detector can not only measure ToF but also record the impact position (X , Y) of each ion. This information allows calculation of the initial position of atoms on the surface of the sample by a reverse projection and reconstruction in three dimensions (3D) of the analyzed volume of the sample. APT allows observation of the structure of matter at the atomic scale in 3D and in the real space. A detailed description of APT can be found in the literature (Gault, Moody, Cairney, & Ringer, 2012; Miller, 2000).

To investigate semiconductor or insulator materials by APT, a nanosecond or femtosecond laser impulsion source needs to be used in order to replace the electric pulses (Kellogg & Tsong, 1980). The choice of a laser pulse with very short duration (femtosecond laser) allows control of atomic evaporation and increases the APT mass resolution (Deconihout et al., 2007). In this work, the laser-assisted wide-angle tomographic atom probe (LAWATAP, CAMECA) was used for SiNW investigation. The laser system is an Ytterbium-doped laser with the impulsion of 400 fs. The total laser power reaches 1 W, and the frequency pulses reach 100 KHz. Three wavelengths were chosen, namely, infrared ($\lambda \sim 1030$ nm), green ($\lambda \sim 515$ nm), and ultraviolet ($\lambda \sim 343$ nm). It has been established that at UV work condition, the characterization of SiNWs has a higher success rate with a good mass resolution ($(M/\Delta M)_{50\%} = 348$).

Considering the analysis temperature for investigation of NWs, four different temperatures were tested, namely, 20, 40, 60, and 80 K using a UV laser source. No temperature dependence of measured dopant (e.g., P and B) concentration in SiNW is found. Note that the voltage applied to tip at higher temperature (80 K) is smaller than the one at lower temperature (20 K), keeping the other experimental conditions constant. Therefore, the sample can be successfully investigated at smaller applied voltages allowing a higher success rate of experiments. Thus, in this work, all the NW investigations are performed at 80 K.

The laser power is also an important parameter that must be chosen appropriately. The choice of an appropriate laser power is done by choosing the pulse fraction. The pulse fraction can be defined as

$$\frac{V_T - V_0}{V_0} \quad (11.2)$$

where V_T is the voltage necessary for atom evaporation without laser pulse and V_0 is the voltage applied on the sample tip to get a given evaporation flux when laser is applied. In this work, all the SiNW investigations are performed using a laser power for a pulse fraction of 20%.

11.3 Basic principle of APT

This section discusses the basic principle of APT and gives a general view of how the atoms in SiNWs are collected, interpreted, and 3D reconstructed.

11.3.1 Time of flight mass spectrometry: chemical identity of atoms

Measuring ToF of an evaporated atom between the tip surface and the detector requires knowing the moment of departure and arrival time. It is therefore essential to control the evaporation of atoms. For this purpose, a direct electric potential V_0 is applied to the tip. In order to trigger the evaporation, an ultrashort electric (V_p) or laser pulses are superimposed at a frequency of several tens of kHz. Note that the use of laser pulses was developed to characterize semiconductor and insulator materials. In the case of metallic samples, an ultrashort electric pulse can be used. Pulses can trigger a timer that will stop when the evaporated atoms are collected by the ion detector located in front of the sample (Figure 11.1). The ToF and the correlated value of the potential applied to the tip are then used to calculate, from the conservation of energy, the mass-to-charge ratio of evaporated and detected atoms. Indeed, using the assumption that the acceleration time of the evaporated atom is negligible compared to the duration of the ToF, it can be written that

$$ne(V_0 - V_p) = \frac{Mv^2}{2} \quad (11.3)$$

where M is the mass of the ion, v is the velocity, n is the charge state, e is the electron charge, V_0 is the direct voltage, and V_p is the pulsed potential, respectively. The mass-to-charge ratio can be then written as

$$\frac{M}{n} = 2e(V_0 + V_p) \left[\frac{t_v}{L} \right]^2 \quad (11.4)$$

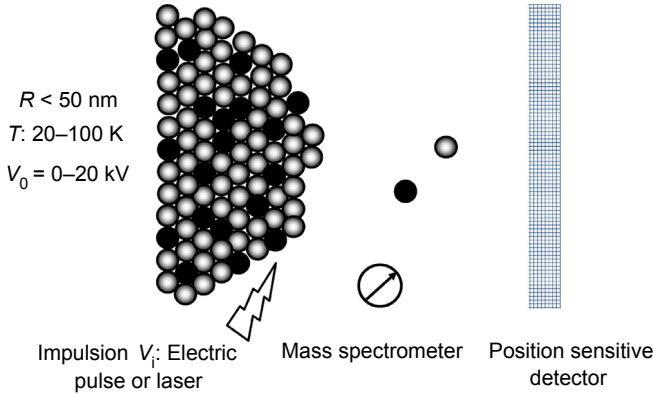


Figure 11.1 Principle of the atom probe tomography. Black and gray represents two different elements. R is the radius of the extremity of the sample.

where t_p is the ToF and L the flight distance. Note that by using laser pulses, V_p is replaced by zero in Eqns (11.3) and (11.4). The value of M/n allows identification of the nature of the detected ions.

During the sample analysis, a mass spectrum is obtained and allows the identification of each chemical element constituting the sample and the number of atoms. The typical mass spectrum of SiNW is shown in Figure 11.2, where the isotopes of Si are clearly distinguished. The atomic concentration C of each element in the analyzed volume is simply obtained by counting the number of atoms in each peak of mass spectrum divided by the total number of collected atoms. The statistical uncertainty of measurement σ is given by

$$2\sigma = \Delta C = 2\sqrt{\frac{C(1-C)}{N}} \quad (11.5)$$

where N is the total number of detected ions.

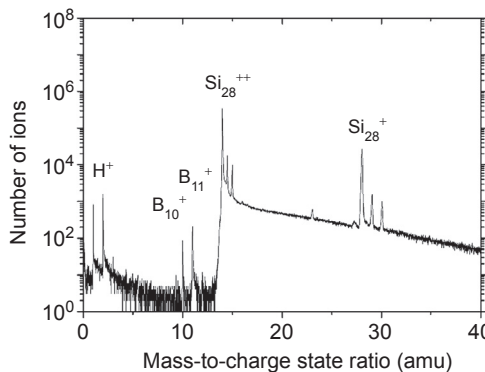


Figure 11.2 Mass-to-charge spectrum of B-doped SiNW. Different isotopes of B and Si peaks have been distinguished.

11.3.2 Analyzed volume

The methods to reconstruct a volume analyzed by APT have been detailed in the literature (Bas, Bostel, Deconihout, & Blavette, 1995). APT is a projection microscope, and the evaporated atoms detected on PSD can be considered as coming from trajectories all crossing at a projection point located at a depth $(1 + m)R$ of the surface of the tip, where m is a dimensionless geometric factor as illustrated in Figure 11.3 (identified to be equal to 0.6 in this work). The coordinates of the ion impacts on the detector allow calculating by reverse projection the original position of atoms on the surface of the tip. The depth of each atom is determined from their order of arrival. We can reconstruct the volume analyzed in three dimensions with a magnification η of the order of 10^7 , which is given by Eqn (11.6):

$$\eta = \frac{L}{(1 + m)R} \quad (11.6)$$

where L is the working distance between NW and PSD, and R is the radius of NW.

The analyzed volume of tip represents the maximum volume that APT can investigate for given experimental conditions. APT being a projection microscope, the analyzed volume is directly related to the analyzed surface, which depends on the tip radius and the distance L . Several protocols have been designed for APT reconstruction (Bas et al., 1995; Geiser et al., 2009). The standard global reconstruction

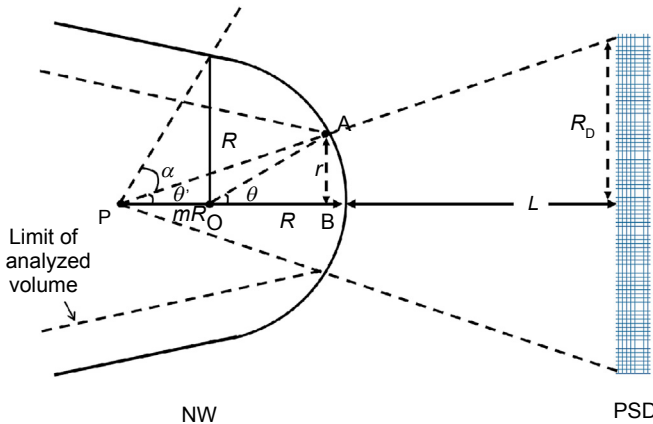


Figure 11.3 Schematic illustration of surface atom projection and analyzed volume when sample (NW) is perpendicular to position sensitive detector (PSD). L is the working distance between NW and PSD, R is the radius of NW, R_D is the radius of PSD. θ is the angle between OA and OB . θ' is the angle between PA and PO . m is a dimensionless geometric factor illustrated as PO . At working distance L for atom probe tomography (APT) with conventional configuration, the sample (NW), the projection and the analyzed volume are presented by solid line, dashed line, and dashed dotted line.

technique of APT is based on a protocol designed by [Bas et al. \(1995\)](#). The calculation here is based on the point projection and geometry model. Considering the geometry of a typical sample (illustrated in [Figure 11.3](#)), we can obtain the relations as follows:

$$OB \tan \theta = (PO + OB) \tan \theta' \quad (11.7)$$

$$\frac{\tan \theta}{\tan \theta'} = \frac{PO + OB}{OB} = \frac{PO}{OB} + 1 = \frac{mR}{R \cos \theta} + 1 \quad (11.8)$$

As θ' and θ are very small, thus.

$$\tan \theta = (m + 1) \tan \theta'$$

$$\theta = (m + 1) \theta'$$

From the point projection, the launch angle θ' is given by the following expression, as illustrated in [Figure 11.3](#):

$$\tan \theta' = \frac{R_D}{(m + 1)R + L} \approx \frac{R_D}{L} \quad (11.9)$$

where R_D is the radius of detector. Thus, the radius of analyzed volume r can be written as

$$r = R \sin \theta = R \sin [(m + 1) \theta'] = R \sin \left[(m + 1) \arctan \frac{R_D}{L} \right] \quad (11.10)$$

where R is the sample radius; θ is the angle between OA and OB; θ' is the angle between PA and PO; m is a dimensionless geometric factor illustrated as PO; R_D is the detector radius; and L is the working distance between sample and detector. From [Eqn \(11.10\)](#), there are two possibilities to increase the analyzed volume considering the instrumentation parameters, namely, decrease the working distance L and increase the radius of detector R_D . However, limitation to increase arises because the mass resolution will decrease L . For example, the most suitable working distance L in the APT used here (CAMEACA LAWATAP) is 98 mm with a detector radius of 38.5 mm. These considerations show why it is not practical to change the instrumentation parameter in order to increase the analyzed volume for having the sample surface information. From [Eqn \(11.10\)](#), the radius r of analyzed volume is calculated to be 0.56 R . It is worth noting that when the sample is perpendicular to PSD, the analyzed volume is only one portion compared to the entire sample tip volume as shown in [Figure 11.3](#). Therefore, the sidewall surface of NW cannot be analyzed. The possible way to obtain information about the surface of the NW sample is to incline it as illustrated in [Figure 11.4](#). In this case, one portion of the tip surface can be analyzed by APT (the shadow region).

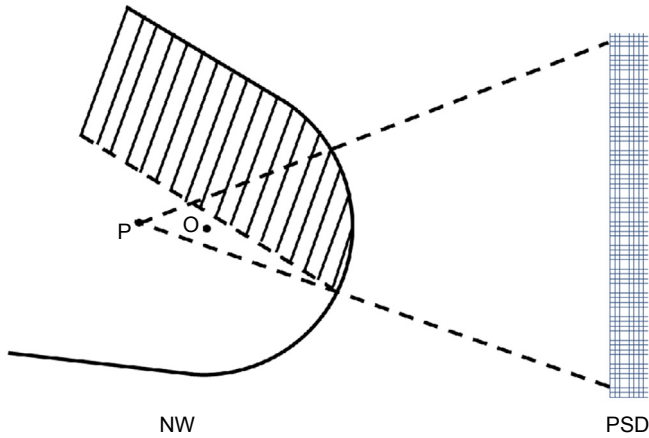


Figure 11.4 Schematic illustration of NW and analyzed volume of atom probe tomography (APT) when NW is inclined in front of position sensitive detector (PSD). The shadow region represents the analyzed volume, which includes the tip surface information.

In order to investigate the NW sidewall, the minimum inclined angle α (illustrated in Figure 11.3) can be calculated as follows:

$$\begin{aligned}
 \tan \alpha &= \tan [(\alpha + \theta') - \theta'] \\
 &= \frac{\tan (\alpha + \theta') - \tan \theta'}{1 + \tan (\alpha + \theta') - \tan \theta'} \\
 &= \frac{1/m - R_D/L}{1 + R_D/mL}
 \end{aligned} \tag{11.11}$$

where, m , R_D , and L are equal to 0.6, 3.85, and 9.8 cm, respectively. Then, α is 38° . If one wants to analyze the sample sidewall surface, the inclined angle must thus be larger than 38° .

11.4 Nanowire sample preparations for atom probe

The main difficulty for the characterization of NWs using the APT technique is related to the sample manipulation and preparation. Different types of sample preparation methods for NW characterization by APT were developed and are described here in detail. Indeed, in this study, the LAWATAP instrument requires mounting a single NW at the top of a support tip. Moreover, the analyses of specific areas of the NW (surface or core) require much attention. Thus, the development of sample preparation methods for APT investigation is the key point in this kind of work. Three different

types of sample preparation methods for NW characterization by APT were developed and are described in this part.

11.4.1 SiNWs grown on Si pillars

The concept of this preparation method consists of the growth of a single SiNW on a micropillar, which is subsequently manipulated in the scanning electron microscope (SEM)-focused ion beam (FIB) dual beam station. This method includes three steps. The first step is the deposition of a few catalyst droplets on the top of an array of Si micropillars. The arrays of Si micropillars ($6 \times 6 \mu\text{m}^2$ and $54 \mu\text{m}$ in height) are fabricated from Si wafers with a [111] orientation (n-type doped ($0.03\text{--}0.05 \Omega \text{m}$)), using the conventional microfabrication process (Levinson, 2005). The second step is the growth of the SiNWs in a CVD growth chamber. The purpose of these two steps is to grow a single NW on the top surface of a micropillar. In the final step, a single micropillar with SiNWs at the top is manipulated and mounted on a preprepared tungsten (W) support tip.

In order to be able to analyze a single SiNW located at the top of a micrometric Si pillar, the surface number density of NWs must be controlled during the growth. In the present case, SiNWs are grown from Au catalyst droplets deposited at the surface of the pillar. Thus, the control of the number density of Au droplets allows the control of the number density and diameter range of SiNWs. Several methods can be used for Au droplets deposition on Si substrate, for example, using Au colloids (Li, Nellist, & Cockayne, 2009; Woodruff, Ratchford, Goldthorpe, McIntyre, & Chidsey, 2007) and Au thin film annealing (Dhalluin et al., 2010; Meng, Shih, & Lee, 2007). In this work, an *in situ* Au evaporation method was used. In order to obtain different Au droplet number densities, the gold droplets were formed directly by gold deposition on a heated Si (111) surface in UHV. Three different substrate temperatures were used: 400, 430, and 460°C using the same deposition pressure of $8\text{--}8.6 \times 10^{-10}$ mbar. The Au droplet density and their diameters can be controlled by the Au evaporation rate and the substrate temperature via the Ostwald ripening process. Following these three conditions, three different densities of gold droplets were obtained. It was shown that the condition with $T = 430^\circ\text{C}$ is the optimal one for the Au droplet deposition (Figure 11.5(a)). Indeed, using this condition, few Au droplets are successfully formed on the top of Si micropillars, allowing the subsequent SiNWs growth for APT analysis. SiNWs can be successfully grown on these Si micropillars (Figure 11.5(b)).

The final step of the procedure is the manipulation of the micropillar itself. This is performed using the conventional lift-out dual beam method. This *in situ* process is realized in a SEM-FIB dual-beam platform. The process can be described as follows: (1) choosing a suitable Si micropillar using microtweezers (Figure 11.5(c)); (2) cutting the Si pillar by using the SEM-FIB dual beam (Figure 11.5(d)); (3) welding of a Si pillar on a preprepared W support tip with gas injection system (GIS) by depositing Pt as the solder in IBID mode (Figure 11.5(e)). A Si pillar with several SiNWs can be prepared using this method (Figure 11.5(e)). For the purpose of APT analysis (only a single SiNW on the Si pillar), the best SiNW (best orientation and length) can be kept and the others have to be eliminated using FIB. Note that great attention must be paid

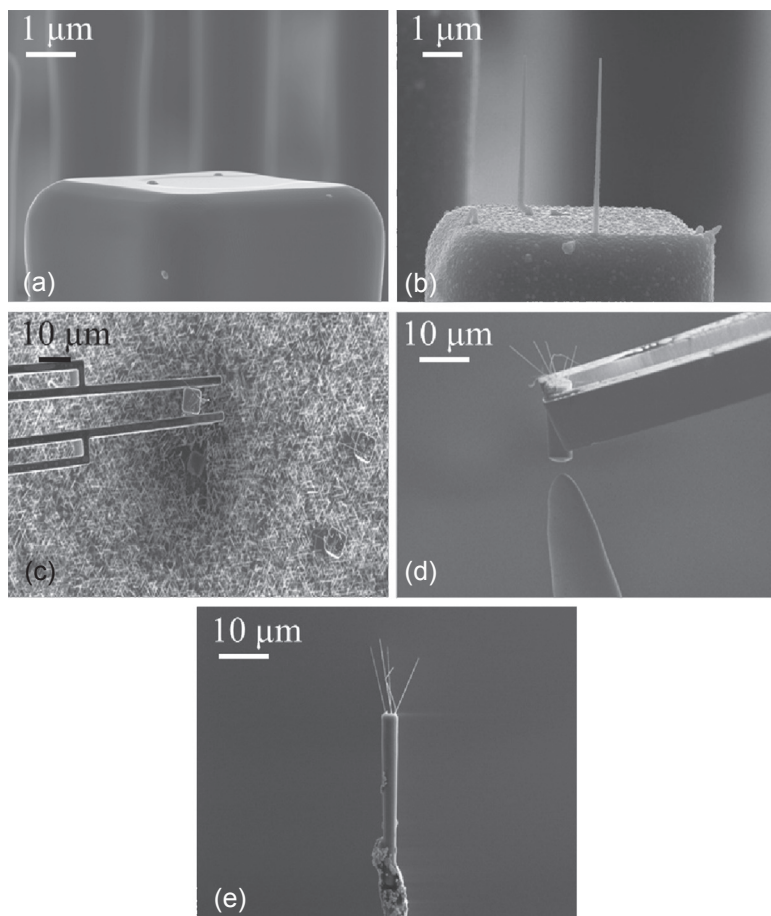


Figure 11.5 SEM images of sample preparation with SiNWs grown on Si micropillars. (a) Au droplets on Si micropillar surface. Two Au droplets are deposited successfully on a Si pillar at $T = 430\text{ }^{\circ}\text{C}$. (b) Growth of SiNWs on Si micropillar using CVD process. The SiNWs are perpendicular to the Si (111) pillar. (c) Lift-out of a Si micropillar with SiNWs grown on the top. Selection of a Si pillar with microtweezers and cutting the Si pillar from the substrate by FIB. (d) Welding the Si pillar with a preprepared W tip by GIS using Pt as solder. (e) Image of the whole structure consisting of NWs, a Si pillar, and a W tip.

to the SiNWs during the FIB process because of the risk of introduction of Ga atoms and their related damages. The as-prepared sample is then introduced in the APT chamber for analysis. This method is very time-consuming due to the involvement of several difficulties such as the low density of SiNWs grown on a single pillar and the manipulation of the Si pillars. Moreover, the APT characterization will begin from the end-growth region of SiNW, which is a specific region nonrepresentative of the whole SiNW due to unstable growth conditions (stop of the gas precursor and temperature decrease of the sample).

11.4.2 Mounting of a single SiNW on a support tip

In this part, an efficient sample preparation method is presented, namely, the direct welding of a single SiNW on a W support tip without the intermediation of *in situ* lift-out technique. Compared to the previous method and with the feedback of experience, this method is more convenient and efficient; it involves only two steps. The first step consists of catching a single SiNW with a W tip under optical microscopy (OM). With this method, either the top end or bottom end can be chosen to perform analysis of SiNW. Indeed, as the morphology of SiNWs is not a perfect cylinder but rather a cone due to tapering effect during the growth (Aella, Ingle, Petuskey, & Picraux, 2007; Chen et al., 2011; Schmid et al., 2008), the top or bottom ends are easily distinguished by SiNW iridescence as shown in Figure 11.6, which is an OM image of SiNWs scratched from the growing Si substrate.

The second step is the welding of SiNW with the W support tip. The selection of an individual SiNW, in specific direction, is performed with a W tip. The contact between the SiNW and the W tip then needs to be reinforced because of the high electrostatic force applied to the SiNW during APT analysis. The reinforcement process is realized by Pt deposition in electron beam-induced deposition (EBID) mode with GIS. Figure 11.7(a) and (b) presents SEM views of SiNW before and after welding by EBID. In this case, the bottom end of the SiNW has been chosen for APT analysis.

SiNWs prepared from this method are usually inclined with respect to the APT detector because of the apex angle of W support tip. Whether SiNW is perpendicular or inclined to APT detector depends on the W tip apex angle θ (Figure 11.7(a)). A very small apex angle allows SiNWs to be perpendicular to the detector, whereas a relative large angle allows a SiNW to be inclined with respect to the detector. The W tip apex angle is roughly controlled during the electropolishing of the support tip. Using this

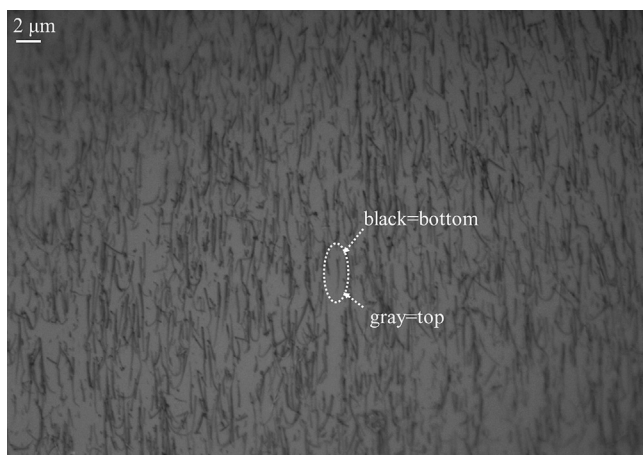


Figure 11.6 Optical microscopy image of horizontal SiNWs scratched on a Si substrate. The change of color along an individual SiNW can be clearly observed because of light iridescence. The colors at top end (Au droplet) and at bottom end are black and gray, respectively.

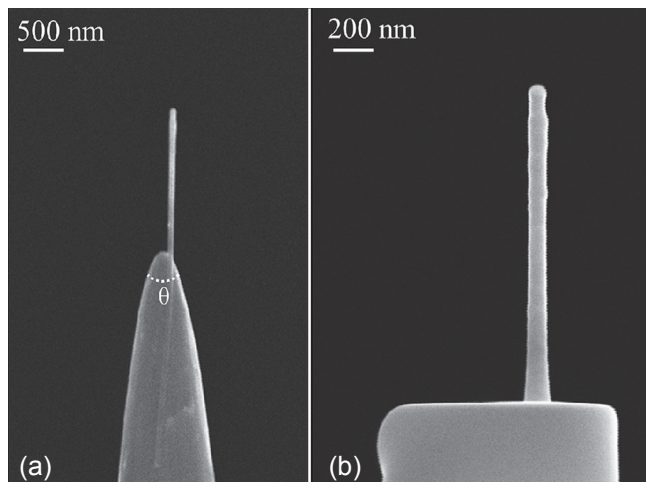


Figure 11.7 SEM view of a SiNW welded on a W tip. (a) Before and (b) after Pt deposition by electron beam-induced deposition (EBID).

convenient and efficient method, NW volume or surface characterization and NW bottom or top characterization by APT are easily performed.

11.4.3 Horizontal Si nanowires for radial characterization

The previous method is efficient for preparing NW for APT. However, it does not allow the radial characterization of NW. The preparation method developed here to analyze the radial direction is also based on the conventional lift-out method but it is more complicated and time-consuming. The procedure of this method is described as follows: (1) A single SiNW is deposited horizontally on a flat Si substrate (Figure 11.8(a)). (2) Deposition of Pt or W as protective layers on top of the SiNW as in the conventional lift-out method (Figure 11.8(b)). The deposition of different materials such as Pt and W is used as the mark layer. Both deposition processes (Pt and W) are achieved by GIS in dual beam SEM platform. (3) The conventional lift-out of a block including the single SiNW (Figure 11.8(c)). (4) Welding the block with a pre-prepared W support tip. As indicated in Figure 11.8(d), a single SiNW is found in the center region of the block. Figure 11.8(e) is a cross-section zoom of a SiNW covered with W. The SiNW cross-section is found to be a hexagon. (5) Annular milling of block using FIB. Figure 11.8(f) presents a multilayer structure comprising Si, W, SiNW, Pt, and W from top to bottom. SiNW must be kept in the center region during FIB process. But this is a very difficult process because of the great difference of Ga atom sputter yields between Si and W at 30 keV Ga ion beam (Nastasi, Mayer, & Hirvonen, 1996). For this reason, the final milling process is no longer homogeneous. There is a great risk of milling the SiNW. Figure 11.8(g) represents one portion of the SiNW after milling. The main difficulty of this method is to place the NW in the center of the APT sample tip without any contamination of Ga atoms.

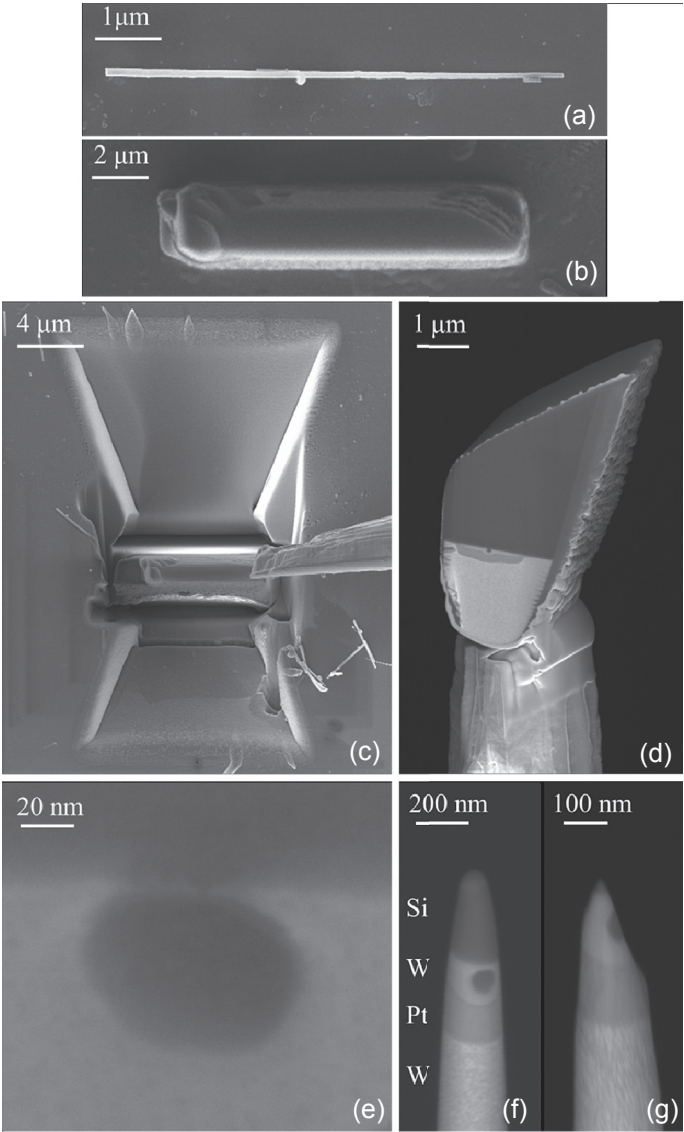


Figure 11.8 SEM images of the processes required for a radial SiNW characterization (a) Deposition of a single SiNW on a Si substrate. (b) Using GIS deposition system, a Pt layer is deposited on the SiNW as a protective layer during the lift-out process. (c) Lift-out of the block containing the single SiNW. (d) Welding of the block with a preprepared W tip. (e) Cross-section view of the SiNW. (f) SEM image of the block after annular milling. SiNW must always be kept in the center region of the block during milling. (g) SEM image of the block with a portion of SiNW.

11.5 Characterization of SiNWs

11.5.1 P-doped SiNWs

As it is naturally an intrinsic material, SiNWs need to be doped for their use in devices such as solar cells. In order to understand the doping process, whatever is the synthesized process, the characterization of an individual SiNW is rather important. As a nano object characterization technique, APT gives us the opportunity to have the information on the dopant distribution and concentration in a single SiNW. In this part, the dopant (P and B) metrology in SiNWs is performed using APT. First of all, P-doped SiNWs are synthesized and characterized. The growth experimental condition is listed in Table 11.1. The total and SiH_4 partial pressure are kept at 10 and 0.65 mbar, respectively. PH_3 is chosen as the dopant precursor to realize P-doped dopant. H_2 is chosen as the carrier gas. SiNWs are synthesized at 500 °C for 20 min.

A SEM image showing a top view of P-doped SiNWs is presented in Figure 11.9(a). In order to perform APT analysis, a single NW needs to be extracted from this NW “forest.” The sample preparation method described previously in Chapter 11.4 is used. A single SiNW is mounted on a W support tip before the welding procedure of Pt as shown in Figure 11.9. It seems that the SiNW is welded inclined on W tip from the side view of SEM. However, the cross-section view of SEM shows that this SiNW is welded on W tip with no inclination from the axis of the overall sample, as shown in Figure 11.9(c), which is a cross-section view of the SiNW shown in Figure 11.9(b). Therefore, the direction of the SiNW is perpendicular to the APT detector.

The 3D reconstruction of an individual P-doped SiNW (with a diameter of 70 nm) is shown in Figure 11.10(a). Si and P atoms are represented by black and gray dots respectively. The arrow indicates SiNW growth direction. Only the NW core region is characterized by APT because SiNW is perpendicular to APT detector (Figure 11.9(c)) due to the limitation explained in Chapter 11.3.2. For clarity, the missing information of NW is illustrated with a grid shell in Figure 11.10(a). The cross-section view of P distribution in SiNW core is presented in Figure 11.10(b). In order to quantitatively investigate the P-doped level in the SiNW, the P concentration distribution in the core region is plotted in Figure 11.10 starting from the SiNW core toward the surface. The concentration of P is measured to be $2.6 \pm 1.5 \times 10^{18}$

Table 11.1 Growth experimental condition of P-doped SiNWs. Phosphine is chosen as the dopant precursor to realize the P-doped SiNWs. Hydrogen is used as the carrier gas

Pressure (mbar)	T (°C)	SiH_4 (mbar)	H_2 (sccm)	PH_3 (sccm)	Time (min)
10	500	0.65	200	0.05	20

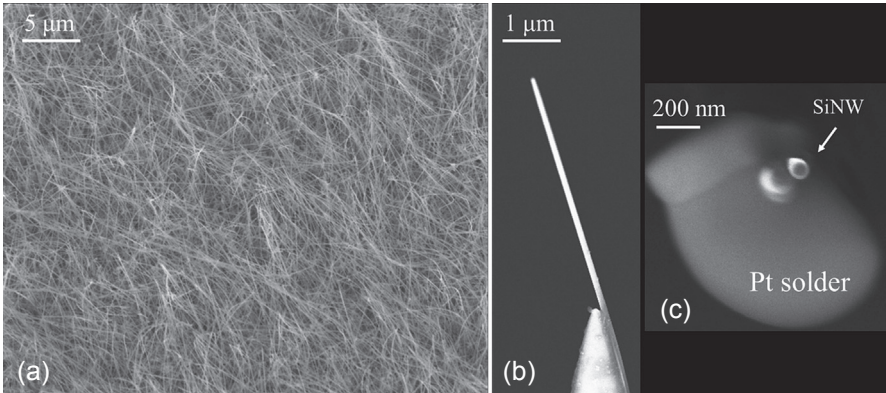


Figure 11.9 SEM image of P-doped SiNWs grown on a Si substrate. (a) Top view of the forest of SiNWs. The growth direction of SiNW is [112]. (b) A single SiNW is mounted on a W support tip. SiNW is chosen directly from the SiNW forest in (a). (c) Cross-section view of SiNW in (b) after welded by Pt.

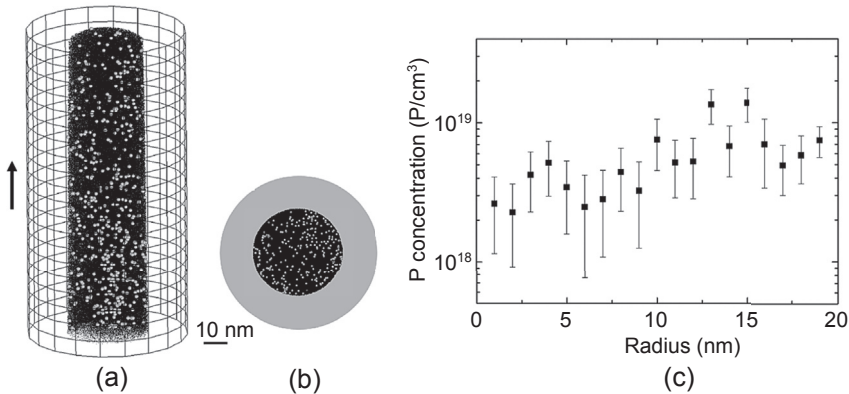


Figure 11.10 3D reconstruction of an individual P-doped SiNW. Si and P atoms are represented by black and gray dots, respectively. (a) The 3D reconstruction of P distribution in SiNW core. The missing NW information during atom probe tomography (APT) investigation is illustrated with a grid shell. Arrow indicates SiNW growth direction. (b) Cross-section view of P distribution in SiNW core. A weak inhomogeneous distribution of P atoms is found. The gray shell represents the missing information. (c) Radial plot of P concentration distribution profile in a P-doped SiNW. P concentration is plotted from the NW interior toward the surface.

P/cm^3 in the NW core and gradually increases toward the NW surface up to P concentration of $7.5 \pm 1.9 \times 10^{18} \text{ P}/\text{cm}^3$ along a distance of 19 nm.

A comparison with secondary ion mass spectrometry measurements performed on a film grown simultaneously with these SiNWs is made (Murthy et al., 2011). It is revealed that the film thickness is similar to the overgrown layer on NW sidewall

and the concentration of P in the film is measured to be 5×10^{19} P/cm³. This P concentration is an order of magnitude higher than the one in the NW core ($2.6 \pm 1.5 \times 10^{18}$ P/cm³). Thus, the P-doped SiNW is expected to exhibit a core-shell structure with a low-doped NW core surrounded by a high-doped shell as for B-doped SiNWs. The radial variation of P concentration can lead to the formation of n-n⁺ core-shell structure. The internal electric field created in this kind of core-shell structure can separate the photoexcited electron-hole pairs efficiently (Murthy et al., 2011).

11.5.2 B-doped SiNWs

The B-doped SiNWs are also characterized by APT and are presented in detail herein. The growth experimental condition of the NWs studied here is listed in Table 11.2. The total and SiH₄ partial pressure is kept at 10 and 0.65 mbar, respectively. The dominant SiNW growth direction is [112] as the precursor pressure is relatively high (Lugstein et al., 2008). For having a B-doped SiNW, B₂H₆ is chosen as the dopant precursor with the ratio SiH₄:B₂H₆ = 4000:1. H₂ is chosen as the carrier gas. SiNWs are synthesized at 500 °C during 20 min. Figure 11.11(a) shows the SEM image of B-doped SiNWs grown on Si wafer. Figure 11.11(b) shows a single B-doped SiNW welded on a W support tip. From the SEM measurement, it is found that the B-doped SiNWs have no tapering during NW growth under these growth conditions.

APT characterizations were performed in the region of the cleaved end of the NWs that were located 6–8 μm from the catalyst droplet. It has a diameter of 58 nm, but only the cylindrical core with a diameter of 30 nm was probed. Figure 11.12(a) shows a 3D reconstruction of the core that extends from the cleavage point over 116 nm along the growth axis. The good crystallinity of the NW core is demonstrated from the resolution of the interplane distance of 0.22 ± 0.01 nm along the [112] growth direction (Figure 11.12(b)). In addition to the Si species, B atoms are also detected. The concentration of B impurities is measured to be 8.1×10^{18} B/cm³ in the center of the SiNW and gradually increases toward the edge (7.1×10^{19} B/cm³) as shown in Figure 11.12(c). Figure 11.12(d) shows the radial and axial B isoconcentration maps in the core of SiNW. The radial B concentration is inhomogeneous in SiNWs.

A quantitative analysis of the B concentration and distribution has also been done and is shown in Figure 11.13. It is indicated in Figure 11.13 that B concentration can

Table 11.2 Growth experimental condition of B-doped SiNWs. Silane is chosen as the precursor gas. Diborane is chosen as the dopant precursor for realizing the B-doped SiNWs. Hydrogen is used as the carrier gas

Pressure (mbar)	<i>T</i> (°C)	SiH ₄ (mbar)	H ₂ (sccm)	B ₂ H ₄ (sccm)	Time (min)
10	500	0.65	200	0.05	20

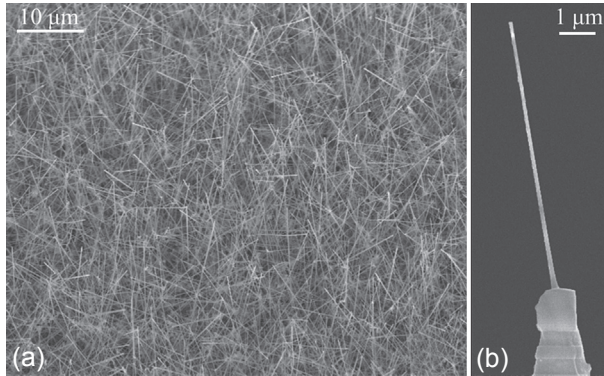


Figure 11.11 SEM image of B-doped SiNWs grown on a Si substrate. (a) Top view of the forest of SiNWs. The growth direction of SiNWs is [112]. (b) A single SiNW is welded on a W support tip. SiNW is randomly chosen from the SiNW forest in (a).

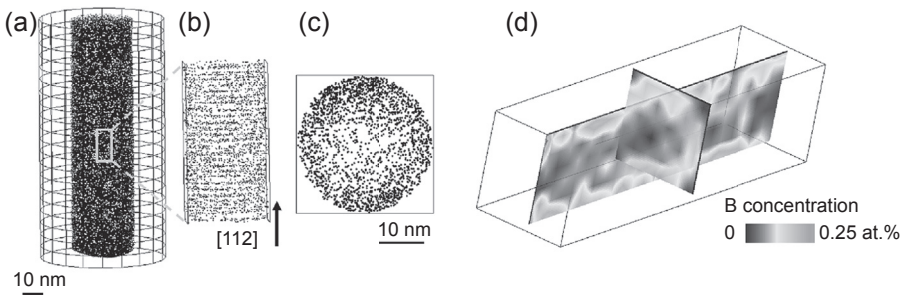


Figure 11.12 Atom probe tomography (APT) investigation of the core region of an individual B-doped Si NW. (a) 3D tomographic reconstruction of B atoms (gray dots) and Si atoms (black matrix) in the core of a 58-nm-diameter Si NW. (b) Enlarged view of the 3D-tomographic reconstruction to show the Si interplane distance of 0.22 ± 0.01 nm. The arrows point in the growth direction. (c) Cross-sectional view of radial B distribution. (d) Radial and axial B isoconcentration in SiNWs.

decrease with one order of magnitude in the SiNW over a radial distance of 15 nm from the surface toward the SiNW core. The B concentration in the core (8.1×10^{18} B/cm³) of the SiNW is much smaller than the estimation given by the flux ratio, 2.5×10^{19} B/cm³ in this growth condition. A theoretical model is presented that is capable of describing the observed spatial inhomogeneity of boron dopant (Chen et al., 2012). We have considered the different kinetic pathways of boron incorporation and discussed the values of diffusion length and diffusion coefficients (D) obtained by fitting the experimental data. Figure 11.13 shows the profile of the average radial boron distribution measured with APT and theoretical curves obtained from the two-dimensional nonstationary diffusion equation at different Dt with $t = 8$ min. The best fit is obtained at $Dt = 20.25$ nm². Consequently, the best fit given in Figure 11.13 corresponds to $D = 4.22 \times 10^{-16}$ cm²/s. This value is much larger than

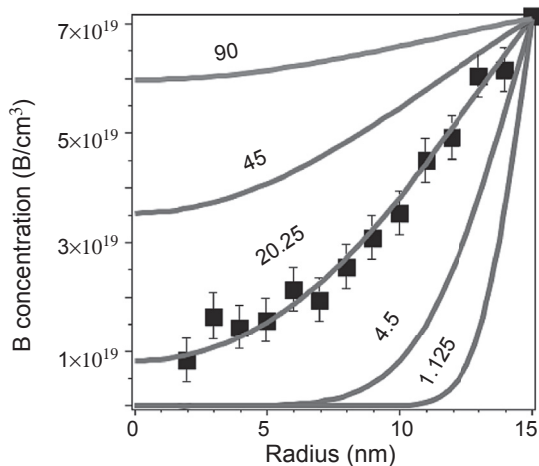


Figure 11.13 Radial concentration profile of B in a SiNW. Measured B concentration (squares) and theoretical concentration profiles (lines) at fixed NW surface concentration $C_0 = 7.1 \times 10^{19}$ B/cm³ (measured by APT) and different Dt (nm²).

the reported bulk diffusivity of B in Si at 500 °C ($\approx 10^{-18}$ cm²/s) (McGuire, 1988, pp. 501–504). With $D = 10^{-18}$ cm²/s, the penetration length of B atoms would be only 1 nm, and the VS mechanism could never work in this case. Therefore, the VS incorporation can explain our data only if the boron diffusivity is dramatically enhanced. The defects in the NW shell could probably enhance the diffusion of the B atoms.

B-doped SiNWs with a significant tapered shape are also investigated in this section. The experimental condition to get this tapering effect is listed in Table 11.3. Silane is also chosen as the Si precursor, but boron trichloride is chosen as the dopant precursor as compared to diborane. Nitrogen is used as the carrier gas. Boron trichloride is diluted with nitrogen with a ratio of 5%. The growth time and temperature are 30 min and 470 °C, respectively. The growth pressure is kept at 149 mbar.

Figure 11.14 is a SEM image of the NWs grown in these conditions. A clear tapering effect is observed. The growth direction of SiNWs is not controlled due to kinks during SiNW growth. The catalyst (Au) droplets can be seen on the top of SiNWs. From the SEM measurements it is shown that the average diameter change with length is estimated to be 48 nm/ μ m. This large tapering effect is mainly due to the NW sidewall lateral growth rather than the gold diffusion, which is inhibited at such high growth pressure. In order to make APT experiments, a single B-doped SiNW is chosen from the SiNW forest and is welded on a W support tip using the same sample preparation method as previously (Figure 11.14(b)). Here, the top end of SiNW is chosen for investigation because the base diameter of NW is very large (≈ 300 nm), which is not suitable for APT characterization. Although we can use FIB to mill the NW with larger diameter, the NW surface information is normally destroyed during the FIB process. Therefore, the end with Au droplet is the best region to analyze.

The 3D APT reconstruction of an individual tapered B-doped SiNW is shown in Figure 11.15(a). Si and B atoms are represented by gray and black dots, respectively. The diameter of the reconstructed volume is not a constant because of the large tapering effect. Here, B atoms are also not homogeneously distributed as in the tapered

Table 11.3 Growth condition of B-doped SiNWs. Silane is also the Si precursor, but boron trichloride is the dopant precursor. Nitrogen is used as the carrier gas. Boron trichloride is diluted with nitrogen with a ratio of 5%

Pressure (mbar)	T ($^{\circ}\text{C}$)	SiH_4 (sccm)	5% $\text{BCl}_3 + \text{N}_2$ (sccm)	Time (min)
149	470	250	200	30

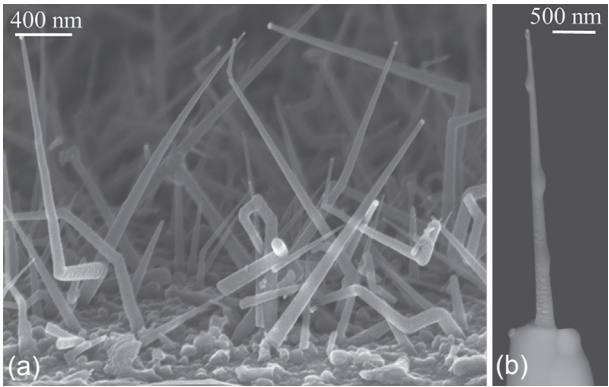


Figure 11.14 SEM image of B-doped SiNWs with large tapering. (a) Side view of the forest of SiNWs with 15° tilt normal to Si substrate. (b) A single SiNW is welded on a W support tip using the sample preparation method described previously. SiNW is chosen directly from the SiNW forest in (a).

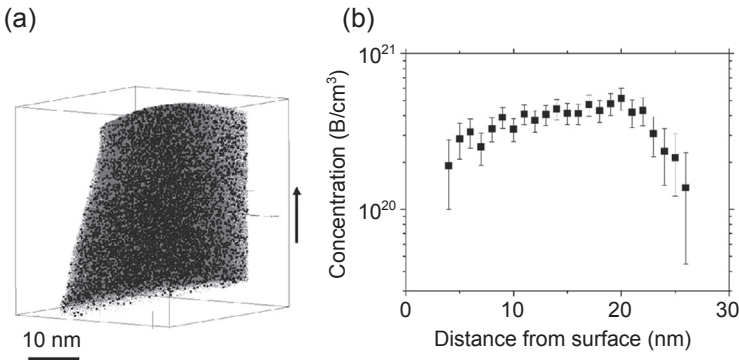


Figure 11.15 (a) 3D reconstruction of an individual tapered B-doped SiNW. Si and B atoms are represented by gray matrix black dots, respectively. The inhomogeneous B atom distribution in SiNW is presented. Arrow indicates SiNW growth direction. (b) Radial B concentration profile in a tapered SiNW. B concentration is plotted from the NW surface to interior.

SiNW. Indeed, owing to the B concentration and distribution, illustrated in Figure 11.15(b), it is clear that, as in the untapered SiNWs (Figure 11.12), B atoms accumulate at SiNW sidewall surfaces. The B concentration in the region of 5–20 nm from the surface is calculated to be $3.57 \pm 0.54 \times 10^{20}$ B/cm³, whereas an estimation of the concentration given by the flux ratio is 1×10^{20} B/cm³ using this growth condition.

The following section is devoted to the investigation of the effect of NW morphology on APT results. The mass spectra from two kinds of B-doped SiNW, without (Figure 11.11) and with (Figure 11.14) tapering, are compared and discussed. Figure 11.16(a) is the mass spectrum of the SiNW without tapering and its schematic illustration. The shank angle θ is assumed to be 0°. A long spectrum thermal tail can be clearly seen following Si peaks. Figure 11.16(b) is the mass spectrum of the SiNW with tapering (48 nm/μm) and its schematic illustration. The shank angle θ is measured to be 2.75°. The thermal tail on the mass spectrum is lower and shorter compared to the one for SiNWs without tapering. One possible reason of the existence of the thermal tail following the Si peak is that Si atoms can also be evaporated between laser pulses despite their femtosecond duration and high frequency. The longer thermal tail in the mass spectrum can degrade the mass resolution. The evaporation of atoms during laser-assisted APT investigation can be considered as a thermal activation (Tsong & Kinkus, 1984). The shape of the NW influences greatly the temperature relaxation of NW between laser pulses. For a SiNW without tapering, it needs more time to cool down to the cryogenic temperature. The simulation from literature shows that a tip with a tapered angle of 4° needs only 50 ns when it is cooled to 70 K compared to 4 μs for a uniform tip (Perea, Wijaya, Lensch-Falk, Hemesath, & Lauhon, 2008). The reason can be explained as follows. The thermal conductivity of SiNW decreases compared to Si bulk (Li et al., 2003). As soon as the heat diffuses from the NW tip (small diameter) to the NW base (large diameter) with a higher thermal conductivity, the cooling rate of NW will increase greatly. By taking advantage of this phenomenon, dependence between sample morphology and mass spectrum quality, NW can be synthesized intentionally with large tapering in order to detect elements with atomic mass larger but near to Si such as P, for example.

As a conclusion, the dopant metrology of P and B atoms in individual SiNWs synthesized by VLS mechanism is achieved with APT. It is found that the dopant atoms such as B and P are distributed nonuniformly in the whole volume of individual SiNWs whatever the NW morphology is. The formation of NW core–shell structure or dopant gradient is due to the underdoped NW core and the overdoped shell. The dopant atoms incorporate into NW principally through the sidewall by a diffusion mechanism with an enhanced diffusivity (much larger as compared to the one in the Si bulk). The influences of NW morphology (without and with tapering) on APT mass spectrum and thus reliability of information are also investigated. It is found that NW with stronger tapering has a better mass resolution compared to the one with weak tapering due to the faster cooling of NWs.

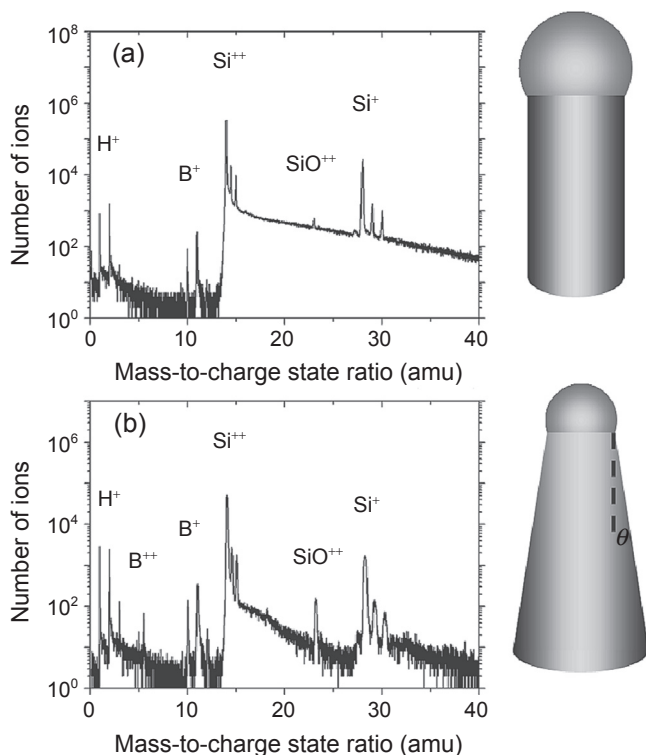


Figure 11.16 Comparison of B-doped SiNW mass spectra. (a) Mass spectrum of a SiNW with a shank angle equal to 0° and its schematic illustration. A spectrum thermal tail can be clearly seen. (b) Mass spectrum of a tapered SiNW and its schematic illustration. The shank angle θ is measured to be 2.75° .

11.6 Summary and perspectives

In summary, APT has been successfully introduced to the different problems linked to SiNW. Even if SiNWs have found applications, more work needs to be accomplished to fully understand their doping and properties. To reach these goals, the use and development of nanoanalytical techniques are essential, among which APT is unique.

Further research should also be undertaken in order to develop the fundamental relationship between the metrology and incorporation of dopants in semiconductor NWs. APT characterization of semiconductor NW is helpful in this domain even if the method for whole volume characterization, for example, needs to be improved and developed.

Acknowledgements

The authors would like to thank Dr Rodrigue Lardé and Dr Emmanuel Cadel of the University of Rouen, Dr Bruno Grandidier of the Université Lille 1, as well as Dr Linwei Yu and Dr Pere Roca i Cabarrocas of École Polytechnique for the results featured in this chapter.

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Optoelectronic properties of semiconductor nanowires

12

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12.1 Introduction

Due to the unique one-dimensional structural characteristics and physical properties, semiconductor nanowires (NWs) have received considerable attention as outstanding potential building blocks for future devices and systems and have been proposed for a variety of functional electronic and optoelectronic components such as light-emitting diodes (Duan, Huang, Agarwal, & Lieber, 2003), field-effect transistors (Duan, Huang, Cui, Wang, & Lieber, 2001; Bakin et al., 2010), photodetectors (PDs) (Paul et al., 2010; Shen, Chen, Bando, Golberg, & Zhu, 2008), and so forth.

In this chapter, we will discuss the optoelectronic properties of semiconductor NWs, the fundament of the NW optoelectronic devices. First, the photoelectric effects of semiconductor will be introduced. Second, the general characterization techniques of the photoelectric effects will be illustrated, involving scanning photocurrent mapping (SPCM) and surface photovoltage (SPV) spectroscopy. Third, the optoelectronic properties of the typical NWs will be briefly reviewed based on material categories, mainly focusing on the photodetection characteristic. Finally, an outlook on future trends is given.

12.1.1 The photoelectric effects of semiconductors

The photoelectric effect was accidentally discovered by Hertz and Hallwachs in 1887–1889 and remained unexplained until Albert Einstein postulated the existence of quanta of light, photons, in 1905, which illustrates that photons when absorbed by an electron near the surface of a material could give the electron enough energy to free it from the material and cause the change of the material's electrical properties. The photoelectric effect includes the following three kinds of phenomena.

12.1.1.1 Photoconductivity

Photoconductivity, as a well-known optical and electrical phenomenon in semiconductor, is an effect that the electrical conductivity increases due to the absorption of light radiation (Bube, 1960, 1992; Rose, 1963). Several mechanisms, such as the absorption of the incident light, the generation of the electron–hole pairs, and the carrier transport, are involved in photoconductivity successively or simultaneously. To cause excitation, the incident light must have energy larger than the bandgap of the

semiconductor so as to raise electrons to the conduction band, or to excite the impurities within the bandgap, and thereby form the electron–hole pairs. The increase of the electrical conductivity depends on the number of the photogenerated electron–hole pairs and the mobility of the carriers, while the duration of the increase is determined by many factors, such as the lifetime of the carriers, the time for the carriers to be trapped. Photoconductivity is the base for the photodetection operation.

12.1.1.2 Photovoltaic effect

This is typically done by using a p–n junction rather than a pure semiconductor due to the presence of potential barrier within p–n junction (Gad et al., 2012; Rittner, 1977; Wang, Pey, Yip, Fitzgerald, & Antoniadis, 2010). As a result of illumination with light featuring energy higher than the energy gap (E_g) of semiconductor, electron–hole pairs generate, and the electrons and holes are separated by the potential barrier to opposite directions, resulting in the potential difference at the two terminals. This phenomenon is called the photovoltaic effect. The voltage across the junction can propel current and convert light into electrical power. Photovoltaic effect is the foundation of the semiconductor solar cells operation.

12.1.1.3 Other photoelectric effects

Other photoelectric effects are caused by radiation of photons with higher frequencies, such as X-rays and gamma rays (Gould & Schröder, 1967; Neutze, Wouts, Spoel, Weckert, & Hajdu, 2000; Stickle, Sobol, & Bomben, 1992). These higher-energy photons can even release electrons near the atomic nucleus. When such an inner electron is ejected, a higher-energy outer electron quickly drops down to fill the vacancy. The excess energy results in the emission of one or more additional electrons from the atom, which is called the Auger effect. This effect is a powerful means of studying atoms and solid surfaces.

Also seen at high photon energies is the Compton effect. When the photon with energy much greater than the binding energy of electrons strikes the semiconductor, they will be scattered. Due to the elastic collision between the photon and electron, energy and momentum are conserved. The photon loses energy to the excited electron. At the same time, a decrease in energy of the photon happens, corresponding to an increased photon wavelength according to Einstein's relation $E = hc/\lambda$. So the scattered radiation is observed to consist of two wavelengths, the original wavelength and an increased wavelength.

12.2 The characterization of photoelectric properties

12.2.1 Characterization of photoconductivity

NW photoconductors (photoresistors) are the simplest configuration to investigate the optoelectronic properties of the NWs. Generally, the NWs are dispersed on an insulating substrate, and metal electrodes are deposited and patterned at the both ends of the

NWs. By supplying a bias voltage to the photoconductor, the current flowing through the device in darkness and under illumination can be measured, and the electrical conductivity can be obtained easily. The magnitude of the change in the conductivity induced by irradiation can be quantified, from which the electronic properties relating to the charge carrier mobility and lifetime can also be analyzed. Varying the state of the irradiation between on and off, the photoresponse characteristics of the material can also be achieved.

Three key parameters are generally employed to evaluate the sensitivity of photoconductors to light: the photoconductive gain G , the responsivity R , and the photosensitivity S (Hu et al., 2013; Murtaza, Nie, Campbell, Bean, & Peticolas, 1996; Peng, Hu, & Fang, 2013). The gain G denotes the number of electrons produced by each absorbed photon in the external circuit, and is often defined as the ratio between the number of collected electrons (N_{el}) to the number of absorbed photons (N_{ph}) per unit time:

$$G = \frac{N_{\text{el}}}{N_{\text{ph}}} = \frac{\tau}{\tau_{\text{tr}}} = \frac{\mu\tau V}{l^2} \quad (12.1)$$

where τ is the lifetime of photogenerated carriers, τ_{tr} is the transit time for carriers between the two electrodes, μ is the carrier mobility, V is the applied bias, and l is the distance between the two electrodes. The responsivity R illustrates the sensitivity of the photoconductor to the incident light and is defined as

$$R(\text{A/W}) = \frac{I_{\text{photo}}}{P_{\text{opt}}} = \eta \left(\frac{q\lambda}{hc} \right) G \quad (12.2)$$

where I_{photo} is the photocurrent, P_{opt} is the power of incident light, η is the quantum efficiency, h is the Planck constant, c is the speed of light, and λ is the incident light wavelength. The photosensitivity (S) is defined as:

$$S = (\sigma_{\text{photo}} - \sigma_{\text{dark}}) / \sigma_{\text{dark}} \quad (12.3)$$

where σ_{photo} and σ_{dark} is the conductance under illumination and darkness, respectively.

12.2.2 Surface photovoltage technique

SPV method is a well-established, contactless technique for the characterization of semiconductors (Lenzmann et al., 2001; Lin, Wang, Zhao, Yang, & Zhang, 2004; Long & Bermudez, 2002; Schroder, 2001). SPV arises from the spatial separation of the photogenerated electron–hole pairs. Therefore, the analysis of the SPV can obtain the transport properties of charge carriers, in addition to the fundamental light absorption properties for semiconductor samples.

Traditionally, SPV can be measured in two arrangements: the Kelvin probe and metal–insulator–semiconductor (MIS). Kelvin probe is usually used to measure the

work function of metal or semiconductors. In this arrangement, the back of the sample should be Ohmically contacted to the metallic reference electrode, and when the electrode is close to the front surface of the sample, the current will be generated in the circuit due to the different work function between the sample and the electrode. Usually, the electrode probe vibrates periodically on the sample surface, causing a steady-state AC current. Consequently, the AC electrical signal will be easily monitored continuously. When the semiconductor is under the super bandgap illumination, the photogenerated electron–hole pairs will be separated spatially by the built-in electric field, resulting in the change of the surface work function. In the absence of the photochemical activity, the photo-induced change of the surface work function is equal to the SPV.

In the MIS arrangement, two electrodes (at least one of them is transparent to act as the light incident electrode) sandwich the sample to form a MIS capacitor. When one side of the sample is excited by the light, the surface work function of the illuminated side is different from that of the back side. The SPV at the semiconductor/insulator interface in the MIS structure can be measured by monitoring the photo-induced voltage changes between the MIS capacitor terminals. It should be noted that in the MIS arrangement, there does not need to be Ohmic contact between the semiconductor and the metal electrode. Usually, the SPV signal is detected by lock-in amplifier, which desires the exciting light to be chopped as a pulsed light so that AC signal is generated.

Additionally, the sensitivity of the method is about 10^8 q/cm², or about one elementary charge per 10^7 surface atoms, which exceeds that of such conventional spectroscopies as XPS and Auger spectroscopy by many orders of magnitude. Therefore, SPV technique has been used widely to study the charge transfer at the surface, interface for bulk and nanostructure semiconductor systems.

12.2.3 Scanning photocurrent microscopy

Scanning photocurrent microscopy (SPCM) is a powerful experimental tool for investigating spatially resolved optoelectronic properties of semiconductors (Kasirga et al., 2012; Verleur, Barker, & Berglund, 1968). In an SPCM setup as shown in Figure 12.1 (Graham & Yu, 2013), a diffraction limited laser spot focused by a high numerical aperture objective lens is scanned on a sample below, while the generated photocurrent in the sample is measured and recorded as a function of excitation position with the two electrodes shorted or electrically biased. An alternative setup is to scan the sample while fixing the laser position. The obtained spatially resolved photocurrent profiles can be used to illustrate the photosensitive regions, defects, and the heterogeneity. The direction of the photocurrent can be used to indicate the local band bending and the local electric field direction. The magnitude of the photocurrent can be used to analyze the internal gain in the PDs and the charge separation efficiency in solar cells (Limpinsel, Wagenpfahl, Mingeback, Deibel, & Dyakonov, 2010; Schwalm et al., 2010). Between 2000 and 2010, SPCM has been extensively used in analyzing semiconductor NWs, carbon nanotubes, and graphene, to extract the carrier diffusion length, internal electrical field, and doping distribution in the materials (LeeEduardo, Balasubramanian, Weitz, Burghard, & Kern, 2008; Mueller,

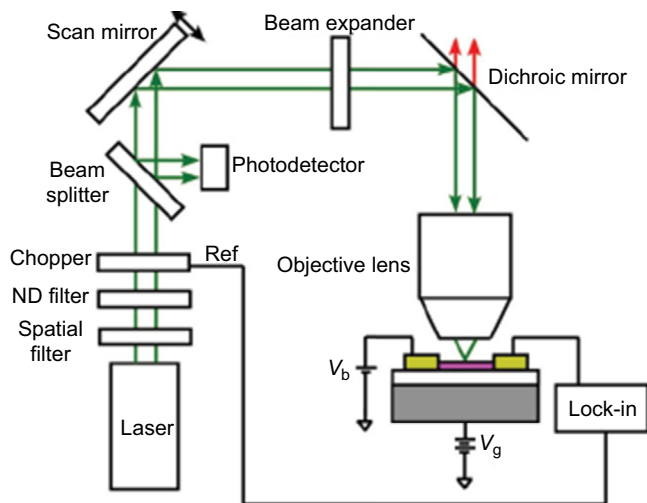


Figure 12.1 A schematic drawing of a scanning photocurrent microscopy setup. Reproduced with permission from [Graham and Yu \(2013\)](#). Copyright 2013.

[Xia, Freitag, Tsang, & Avouris, 2009](#); [Weiss et al., 2012](#)). It must be noted that the metal–semiconductor contacts in the measured device play an important role in the photocurrent profile, and at least one Schottky contact is prerequisite to obtain the correct minority carrier diffusion length.

As the need for complete understanding of the characteristics of the photoelectric material increases, developments in experiment techniques emerge endlessly, such as near-field scanning optical microscopes ([Rauhut et al., 2012](#)), electron beam induced current ([Donolato, 1983](#); [Luke, Roos, von, & Cheng, 1985](#)), and two-photon optical beam induced current ([Parkinson et al., 2013](#)), which are likely to expand the realm of SPCM. These common photocurrent studies are generally limited to timescales exceeding 10 ps, since the electronic equipment cannot produce faster trigger signals and detect the transients. But, in semiconductor NW devices, it has been pointed out that the carrier recombination and relaxation processes can occur on much faster timescales. Therefore, the combination of ultrafast spectroscopy with high spatial resolution emerged, called the pump–probe method.

For pump–probe measurement, as shown in [Figure 12.2](#), the laser pulse is split into two optical paths of equal length at a beam splitter ([Sun et al., 2013](#)). One path is used as the probe for regular SPM, which can be scanned on the sample by using a two-dimensional scanning mirror. The other path is used as pump beam. The delay time between the two pulses is precisely controlled by a delay stage in the pump beam path. The two pulses are recombined at another beam splitter and focused by a microscope objective onto the sample. Measuring the photocurrent as a function of the delay time at the field probe can obtain the information on the optoelectronic response of the sample with a picosecond time resolution. Ultrafast pump–probe technique has been

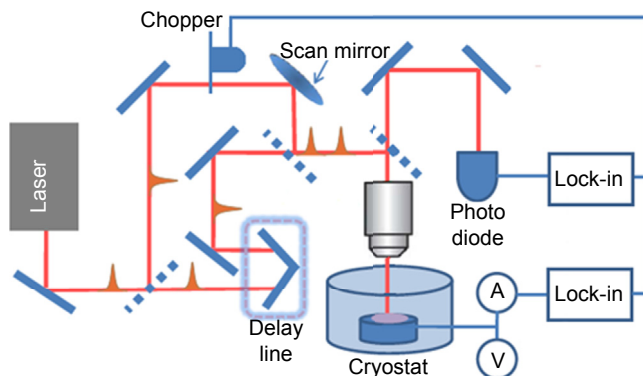


Figure 12.2 Schematic of experimental setup of pump–probe measurements. Reproduced with permission from [Sun et al. \(2013\)](#). Copyright 2012, Nature Publishing Group.

employed to exploit the photocurrent mechanisms and the fundamental operation speed limit in GaAs NWs ([Prechtel, Padilla et al., 2012](#); [Prechtel, Manus, Schuh, Wegscheider, & Holleitner, 2010](#)), carbon nanotubes ([Prechtel et al., 2011](#)), and graphene ([Sun et al., 2013](#); [Prechtel, Song et al., 2012](#)). The obtained results are useful for the design of NW-based optoelectronic devices.

12.3 The optoelectronic properties of the NWs

The photovoltaic properties of the NWs will be dealt with in another chapter, so in this chapter, we will mainly focus on the photoconductivity properties of NW-based PDs. Both the intrinsic material properties (e.g., the bandgap, carrier density, and mobility) and the device dimension play a vital role in determining the photoresponse of NW photoconductors. Here we will focus on the intrinsic material properties based on material categories.

12.3.1 Group IV

The most widely used Group IV semiconductors in devices include Si and Ge. Here we will discuss the optoelectronic properties of Si, Ge, and $\text{Si}_{1-x}\text{Ge}_x$ NWs.

12.3.1.1 Silicon

Silicon (Si) has been the material for visible light detection due to the 1.12 eV bandgap at 300 K and the compatibility with CMOS processing ([Bleka, Murin, Monakhov, Avset, & Svensson, 2008](#); [Gill, Hall, & MacEvoy, 1997](#); [Myers, Farrell, Karger, Carey, & Mazur, 2006](#); [Zhao, Green, & Wang, 2002](#)). The optoelectronic properties of Si NWs, achieved by chemical synthesis and etch-back methods, have been intensively studied by constructing photoconductors ([Hannon, Kodambaka, Ross, & Tromp, 2006](#); [Li, Qian, Xiang, & Lieber, 2006](#)).

The exciting wavelength dependence of Si NWs, which were synthesized by thermal chemical vapor deposition (CVD), was studied by using the conventional photoresistor structure as shown in Figure 12.3, where the Au/Ti multilayer electrodes were formed by lithography (Kim et al., 2006). The photocurrent–voltage curves were measured under the illumination of 325- or 633-nm-wavelength laser. The results of the undoped Si NW were shown in Figure 12.3. Nonlinearity of the I – V curves is ascribed to the Schottky contact between the electrodes and the NWs. The current under illumination is significantly larger than that in darkness. And despite the lower energy of the 633-nm-wavelength light (1.96 eV), its induced photocurrent is larger than that by the 325-nm light, which can be explained by the bandgap structure as follows: when the Si NWs are illuminated by the light with energy in the range from the indirect bandgap 1.12 eV to the direct bandgap 3.34 eV at 300 K, the electrons will be raised to an X point in the conduction band with the assistance of electrons. While, when stricken by the light with energy higher than the direct bandgap 3.34 eV at 300 K, the electrons will be excited from the valence band to the conduction band at a Γ point in the direct bandgap, and then move to an X point with thermal loss, which results in the lower photocurrent.

The doping effect on the photoresponse of Si NW was investigated as shown in Figure 12.4. From Figure 12.4(a), it can be seen that the undoped Si NWs have response time and recovery time as short as 100 μ s. But in the doped Si NWs, the photogenerated charge carriers will be trapped and detrapped by the midgap states introduced by the dopant, which will slower the photoresponse, as shown in Figure 12.4(b) and (c).

Zhang et al. investigated the phototransistive gain of Si NWs, as shown in Figure 12.5. The measured gain is as high as 35,000 at the low light intensity and saturates at high light intensities (Zhang et al., 2008). The large gain is attributed to the enhancement of carrier lifetime, which is due to the spatial charge separation induced by the built-in lateral field between the trapped carriers at the surface and the ionized impurities in the NW.

12.3.1.2 Germanium

Germanium (Ge) is a widely used semiconductor with an indirect bandgap of 0.66 eV at 300 K (Fang, Föll, & Carstensen, 2006; Logan & Peng, 2009; Nguyen, Ng, & Meyyappan, 2005; Polyakov et al., 2006; Wu, Punchaipetch, Wallace, & Coffey, 2004). In the past few years, several research groups have employed the advantages of Ge NWs, such as high carrier mobility and the ease of synthesis, in PDs and various other devices (Cao et al., 2009; Kim et al., 2011; Tang et al., 2008; Wu et al., 2004).

Four kinds of Ge NW arrays, with the mean diameter of 50 and 100 nm, and the top electrodes of tin-doped indium tin oxide (ITO) and semitransparent Au electrodes, were fabricated to study the process dependence of the optoelectronic properties. The NWs were deposited within the pores of anodized aluminum oxide (AAO) membranes by using the method illustrated in Polyakov et al. (2006). Figure 12.6 shows the photoconductivity measurement set, and the incident pulse Ar laser (wavelength: 457–514 nm, pulse: 0.5 ms) had an intensity of 800 mW/cm².

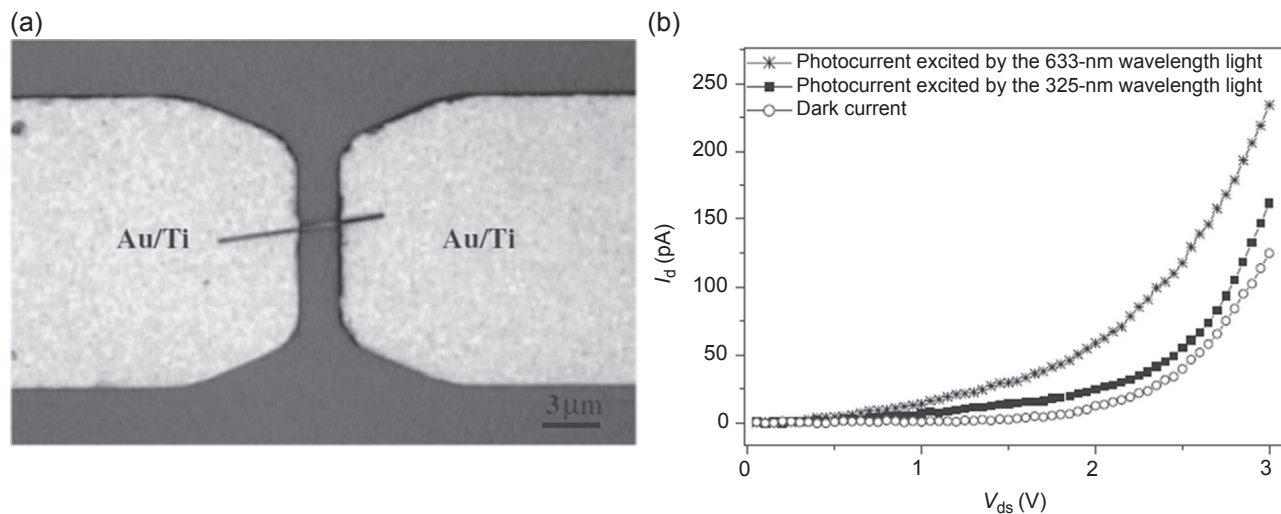


Figure 12.3 Optical microscope image (a) of a single-crystalline Si nanowire between two Ti/Au electrodes on a SiO_2/Si substrate, and I – V curves (b) for the single-crystalline Si nanowire in the dark and under the illumination of the 325- and 633-nm-wavelength light. Reproduced with permission from [Kim et al. \(2006\)](#). Copyright 2006, Japan Society of Applied Physics.

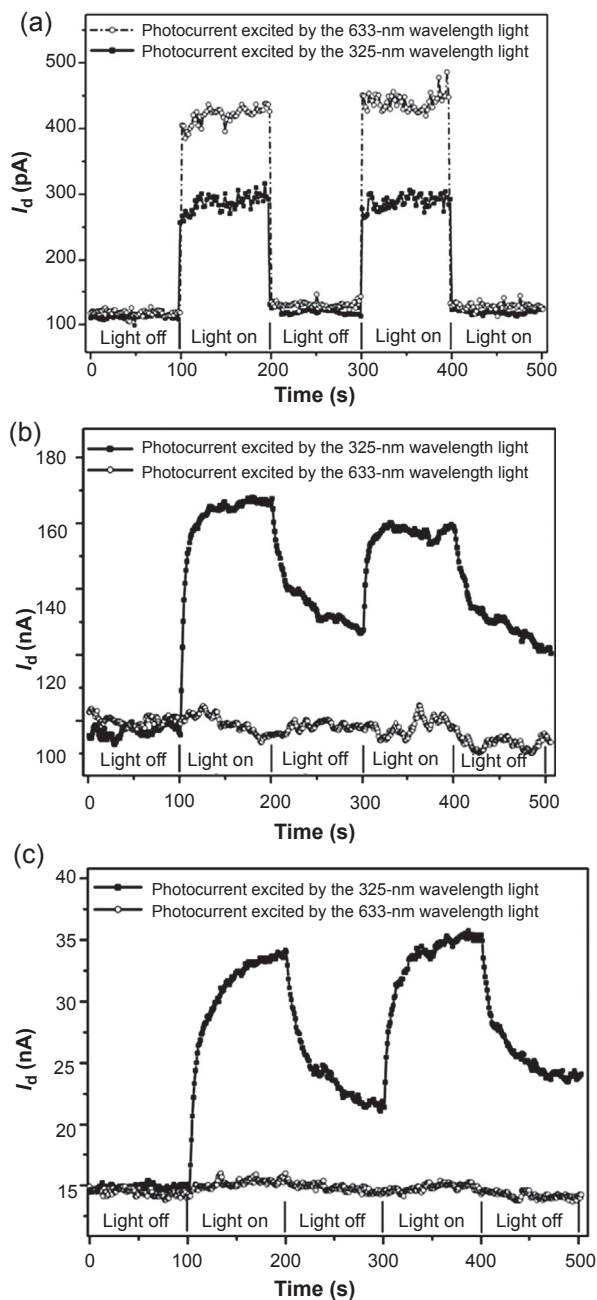


Figure 12.4 Time-dependent photocurrents of the intrinsic (a), n-doped (b), and p-doped (c), Si nanowire under the illumination of the 325- and 633-nm-wavelength light. The light was switched on and off per 100 s in air at room temperature at a bias voltage of 3 V. Reproduced with permission from [Kim et al. \(2006\)](#). Copyright 2006, Japan Society of Applied Physics.

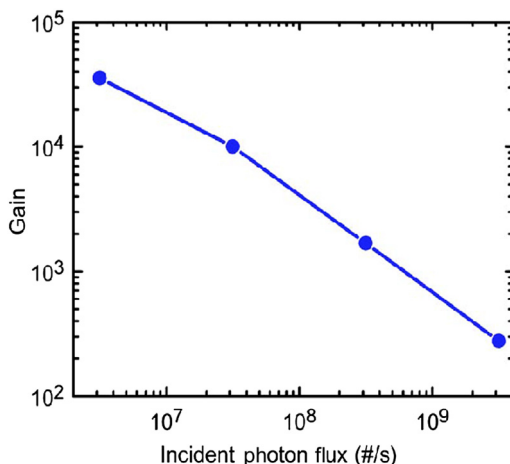


Figure 12.5 Gain versus estimated photon flux incident on the exposed NW area for this NW device biased at 0.5 V.

Reproduced with permission from [Zhang et al. \(2008\)](#). Copyright 2008, American Institute of Physics.

The dark and photo IV characteristics of the different Ge NW arrays were measured as shown in [Figure 12.7](#) ([Polyakov et al., 2006](#)). Polishing and etching of the samples can increase the exposed contact area, resulting in a significant reduction of the resistance, compared to the “polishing only” samples as shown in [Figure 12.7\(a\)](#). The partial oxidation of the NWs in the oxygen-containing atmosphere during the formation of ITO electrodes increases the resistance, which induces less current as shown in [Figure 12.7\(b\)](#). The lower transparency of the top Au electrodes leads to the smaller photocurrent/dark current ratios in Au-NW samples (3–5%) as shown in [Figure 12.7\(c\) and \(d\)](#).

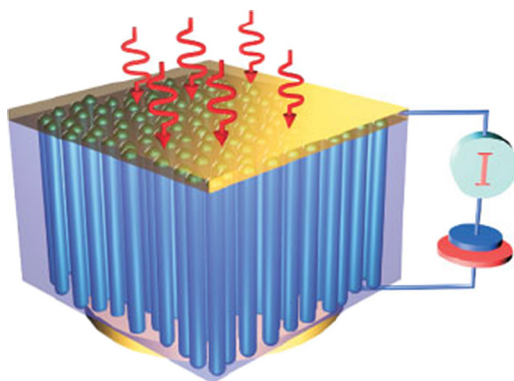


Figure 12.6 Schematic drawing of the photoconductivity measurement assembly.

Reproduced with permission from [Polyakov et al. \(2006\)](#). Copyright 2006, Wiley-VCH.

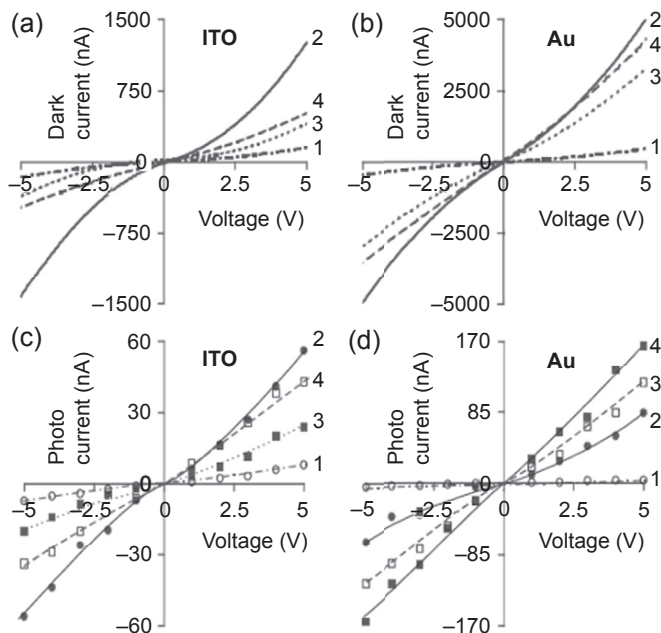


Figure 12.7 *I*-*V* characteristics of Ge nanowire–anodized aluminum oxide (AAO) samples with mean diameters of 50 and 100 nm: (a) dark currents from deposited indium tin oxide (ITO) top electrodes, (b) dark currents from semitransparent Au top electrodes (thickness c. 25 nm), (c) photocurrent, I_{ph} from deposited ITO electrodes, and (d) I_{ph} from semitransparent Au electrodes obtained using a laser intensity of 800 mW/cm² measured after 50 ms illumination. Plots 1 and 3: *I*-*V* data from Ge nanowires with mean diameters of 50 and 100 nm, respectively, after polishing of the AAO surface before contact deposition. Plots 2 and 4: *I*-*V* data from Ge nanowires with mean diameters of 50 and 100 nm, respectively, after polishing and etching of the AAO membranes before electrode deposition.

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The photocurrent dynamics, which were measured at room temperature, shown in Figure 12.8 indicate that the Ge NW array exhibits photocurrent kinetics on the millisecond timescale, which is much longer than bulk Ge.

The spatial dependence of the optoelectronic properties due to the contacts between the electrodes and NWs were also studied by employing the structure as shown in Figure 12.9(a), where Ge NW with the length of 2 μ m was synthesized by vapor–liquid–solid (VLS) CVD, and the Ti electrodes were patterned by lithography and liftoff. The NW device was illuminated by a scanning laser beam with a diameter of 500 nm at half maximum (Ahn & park, 2007). The scanning photocurrent, as a function of the laser spot position, was recorded, shown in Figure 12.9(b). The localized current spots were found near the drain and source electrodes, indicating higher sensitivities near the contacts, which was contributed to the energy bending due to the Schottky contact as shown in the inset. The relationship between the photocurrent at the drain electrode and the light intensity was shown

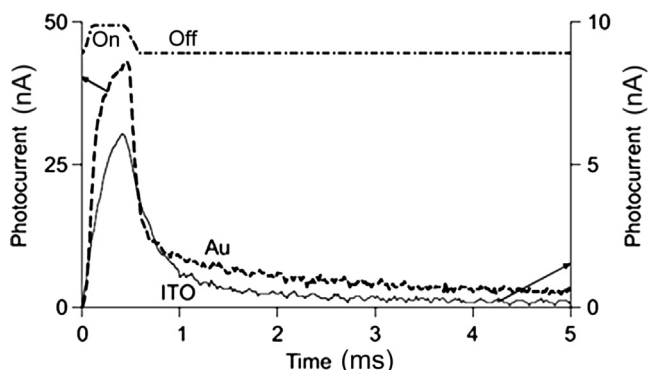


Figure 12.8 The photocurrent dynamics of etched arrays of Ge nanowires with mean diameters of 100 nm at 0.5 ms laser pulse illumination for Au and indium tin oxide (ITO) electrodes. Reproduced with permission from Polyakov et al. (2006). Copyright 2006, Wiley-VCH.

in log–log plot of Figure 12.9(c), indicating that Ge NW exhibits sensitive photo-response at low light intensity due to the internal gain mechanism.

12.3.1.3 $\text{Si}_{1-x}\text{Ge}_x$

The single NW-based composition grading of $\text{Si}_{1-x}\text{Ge}_x$ alloys was used to fabricate on-wire high efficiency PDs to investigate the optoelectronic properties (Li, Chua, & Fitzgerald, 2003; Pike, Ksendzov, Fathauer, & George, 1993; Robbins, Stanaway,

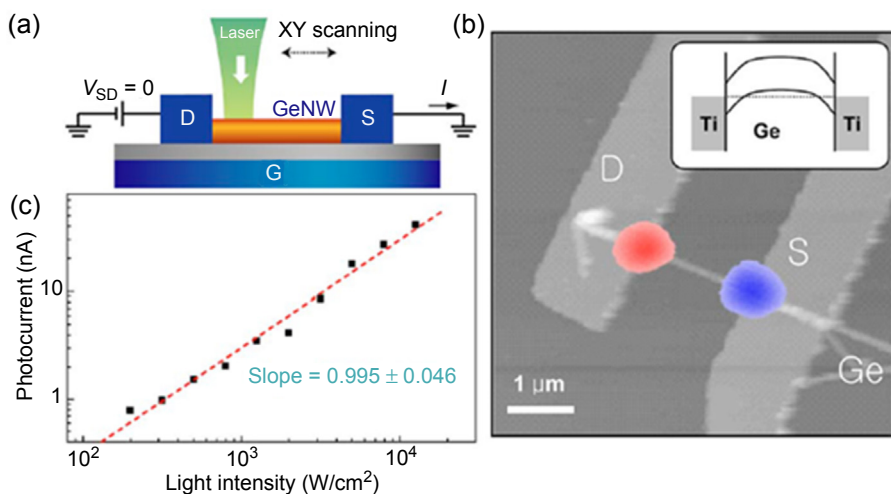


Figure 12.9 (a) Schematic of the scanning photocurrent (SPC) measurement setup. (b) SPC image, overlaid on an AFM image for a 2- μm -long Ge NW at $V_G = V_{SD} = 0$. (c) Magnitude of SPC at drain electrode as a function of the light intensity.

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Leong, Glasper, & Pickering, 1995; Roucka et al., 2005; Souifi et al., 1992). Local carrier transport of composition-graded Si:Ge alloys were investigated by a multiterminal contacted bandgap-graded $\text{Si}_{1-x}\text{Ge}_x$ NW. Each segment on the NW had an axially compositions variation of $\sim 15\%$ within a length of ~ 3.7 mm. With the Ge concentration gradually increasing, the resistivity of NWs decreases over three orders of magnitude due to the nature of bandgap variation in the composition gradient $\text{Si}_{1-x}\text{Ge}_x$ NW.

A super continuum laser source combined with a monochromator was used to do the photocurrent (I_{ph}) measurements. The laser beam was locally focused on a composition-graded $\text{Si}_{1-x}\text{Ge}_x$ NW along the entire length (Kim et al., 2011). The measured I_{ph} of each spot on the graded $\text{Si}_{1-x}\text{Ge}_x$ NW progressively shifted to the lower photon energy with the decreased content of Ge. Figure 12.10 shows the representative I_{ph} images measured on the multiterminal NW PDs of D1–D3 (device 1, 2, and 3) by scanning the photocurrent, where the composition gradient Si:Ge alloy is

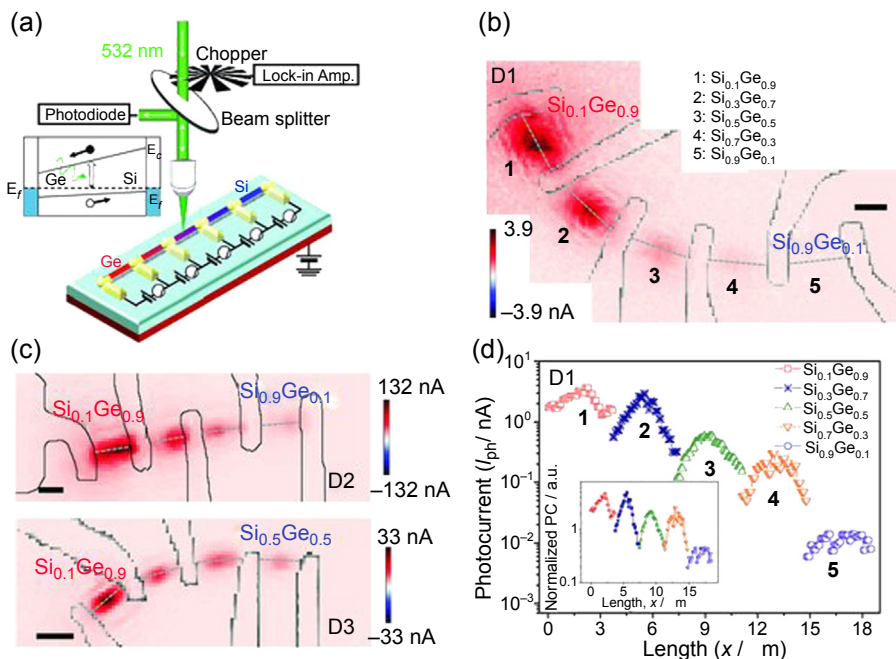


Figure 12.10 (a) Schematics of the SPCM (spectra photocurrent measurements) setup for the axially composition modulated $\text{Si}_{1-x}\text{Ge}_x$ NW multiterminal photodetectors. The inset illustrates the expected band diagram of NW channel. (b, c) SPCM images of (b) D1 and (c) D2–D3 at $V = 1$ V overlaid on the reflection images in gray. The marked numbers represent various Si:Ge compositions, as labeled, and the scale bar is 2 μm . (d) Photocurrent line profiles taken along the channel of (b) at 1 V bias voltage. The inset shows the normalized photocurrent by the effectively absorbed photon flux, as detailed in the main text. All scanning photocurrent data were taken by a lock-in current measurement, relayed with the chopper of 10 kHz. Reproduced with permission from Kim et al. (2011). Copyright 2011, Wiley-VCH.

modulated axially by the labeled amount. The I_{ph} intensity is observed to be the maximum value at the Ge-rich segment, and it is progressively diminished from one end of the NW to the other end, as the Ge content is gradually diluted. The I_{ph} magnitude peak value in each channel gradually varies by roughly one order. The I_{ph} intensity profiles shown in Figure 12.10(d) were extracted from D1. The I_{ph} peak values are commonly observed in the stems of the NW instead of the contact region, which confirms that the photocarrier transport is mainly governed by drift along the channel band tilting instead of a local bending at the contact.

12.3.2 Group II–VI

II–VI semiconductors are widely used in photonics and optoelectronics due to their direct bandgap. Various II–VI semiconductor NWs have been synthesized and show significant optoelectronic properties.

12.3.2.1 Cadmium sulfide

Cadmium sulfide (CdS) is an important direct intermediate bandgap (2.42 eV at 300 K) with excellent thermal and chemical stability and strong optical absorption and is used in solar cells, PDs, light emitting diodes, and lasers (Chuu & Dai, 1992; Jie et al., 2006; Leheny, Shaklee, Ippen, Nahory, & Shay, 1970; Li et al., 2010; Liu et al., 2004; Ozaki, Peebles, Weinberger, Heeger, & MacDiarmid, 1980). Here, we will discuss its optoelectronic properties, including photoconductivity, photon response, doping effect, and so on.

The chlorine-doping effect on the photoconductivity of CdS NW was investigated by Wu et al. (2010). Chlorine-doped NWs with different doping concentrations were synthesized by adjusting the vapor pressure of n-type dopant CdCl_2 , which was realized by controlling of dopant source evaporation temperature. The impact of doping was investigated by comparing the photoconductive properties of doped NWs and intrinsic ones. By controlling the Cl-doping concentration, the conductivity of CdS NWs can be largely enhanced, due to the introduction of shallow donor levels under the conduction band by Cl dopant. Under white light illumination, the conductivity of the doped samples showed a significant increase up to three to four orders of magnitude. At the same time, both Cl-doped and intrinsic CdS NWs exhibited excellent stability and reproducibility with a fast response time shorter than 1 s, which indicates the high crystal quality of the doped NWs. Due to the presence of deep level trap states in the doped NWs, which can prevent the electron–hole recombination and greatly prolong the lifetime of the photocarriers, the responsivity (R), photocurrent gain, and the $I_{\text{light}}/I_{\text{dark}}$ ratio were also enhanced in the doped samples. However, The $I_{\text{light}}/I_{\text{dark}}$ ratios degrade with higher doping concentration, indicating that a balance must be taken between the doping concentration and devices performance. These results illustrate that the photoconductivity properties can be significantly enhanced by rationally doping.

The effect of contacts on the photon detection properties of CdS NWs was studied by Wang's group (Wei et al., 2010). The Ohmic contact in the device shown in the inset of Figure 12.11(a) was realized by Ga doping in the Pt electrodes. Without Ga

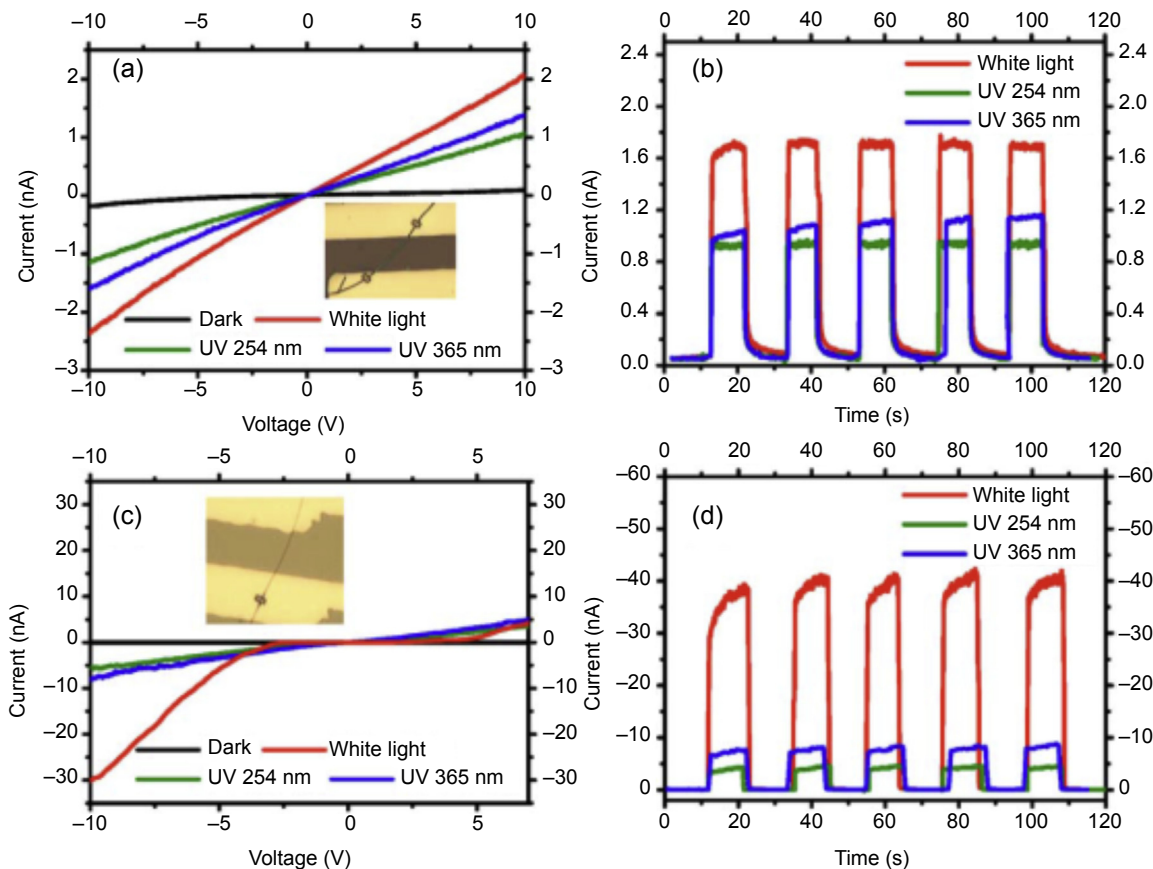


Figure 12.11 (a) I – V characteristics of CdS NW-based Ohmic contact-based devices (OCD) under four different light illumination conditions. The inset shows the optical microscopy (OM) image of the OCD. (b) The response curves of the OCD under illumination of three different light sources. (c) I – V characteristics of CdS NW-based Schottky contact devices (SCD) under four different light illumination conditions. The inset shows the OM image of the SCD. (d) The response curves of the SCD under illumination of three different light sources.

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doping, due to the high work function of Pt, a Schottky contact formed, as shown in Figure 12.11(c). The adsorption of the oxygen in the air will happen at the Schottky contact as well as on the NW surface. When excited by a light, the electron–hole pairs generate, and the holes will be combined by the adsorbed negatively charged oxygen ions, which results in the reduced electron depletion layer thickness and the lowered Schottky barrier height. Thus, the largely enhanced photo detection sensitivities are achieved in the Schottky contact-based devices as shown in Figure 12.11(d). The reset time of the Schottky-based device (320 mS) is shorter than that of Ohmic-based devices (572 mS) shown in Figure 12.11(b).

The mobility-lifetime product, which is the average length a carrier moves per unit field, is an important parameter for the charge collecting in optoelectronic devices. The quantitative determinations of the carrier mobility-lifetime product for electrons and holes in CdS NWs were reported by Gu, Romankiewicz, David, Lensch, and Lauhon (2006). They fabricated photoresistors with Ti electrodes based on VLS-synthesized CdS NWs. Ohmic contacts were formed by bombarding the contacts region with Ar ions before Ti evaporation. Scanning photocurrent microscopy (SPCM) was used to analyze the spatial variations in the photoconductivity.

Figure 12.12(a) and (b) shows the structure of the CdS NW device and the photocurrent as a function of the illuminating beam position, respectively. Due to the Ohmic contacts, the current peak was in the local photocurrent images at all biases, which is different from the devices with Schottky contacts. The data in the SPCM image were extracted to analyze the carrier collection efficiency versus injection position, as shown in Figure 12.13, from which, the peak shifted to the hole collector can be observed. When the injection point moved away in either direction, due to the enhanced probability of carrier recombination, the photocurrent decreased exponentially. The drift/diffusion length of the holes and electrons in CdS NWs was extracted by fitting the left and right side of the photocurrent profile, respectively. It turned out that the drift length of electrons (1.47 μm) is larger than that of holes (0.65 μm). Combining with the Einstein relation, the mobility-lifetime product

$$\mu\tau^* = \left(\frac{q}{k_B T} \right) L^2 \quad (12.4)$$

was obtained, as shown in Figure 12.13(b), from which it is found that the electron transport is much more efficient than hole transport, and the carrier lifetime in CdS NWs is longer than in bulk CdS.

12.3.2.2 Cadmium selenide

Cadmium selenide (CdSe), another well-known direct bandgap (1.74 eV at 300 K) II–VI semiconductor, which favors the absorption over a wide range in the visible spectrum, has been exploited as a potential material for applications in optoelectronics (Chestnoy, Hull, & Brus, 1986; Lunz et al., 1996; Nair, Nair, Zingaro, & Meyers, 1993; Peng, Schlamp, Kadavanich, & Alivisatos, 1997; Samarth et al., 1989; Yamamoto, Sasamoto, & Inagaki, 1998; Yu et al., 2003). The optoelectronic properties of CdSe NWs have been reported by several groups.

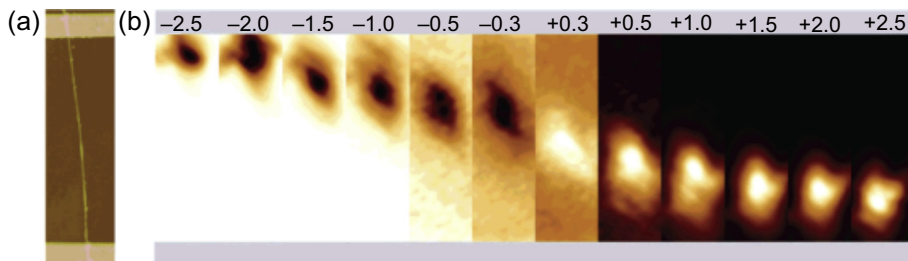


Figure 12.12 SPCM imaging of a CdS nanowire device with two Ohmic contacts at the top and bottom. (a) Atomic force microscope topographic image of CdS nanowire and electrodes. The electrode width is 1 μm , and the device length is 11 μm . (b) Sequence of SPCM images with the top electrode biased as indicated. The peak photocurrent, whether positive or negative, is always shifted toward the hole collector. The peak shift saturates for $|V_{2.5} < |V$. Reproduced with permission from [Gu et al. \(2006\)](#). Copyright 2006, American Chemical Society.

[Kung, Veer, Yang, Donovan, and Penner \(2010\)](#) prepared nanocrystalline CdSe (nc-CdSe) NWs array with a pitch of 5 μm , as shown in [Figure 12.14\(a\)](#), by using the lithographically patterned nanowire electrodeposition method. Gold electrodes with a thickness of 40 nm and a distance of 5 μm were evaporated to form electrical

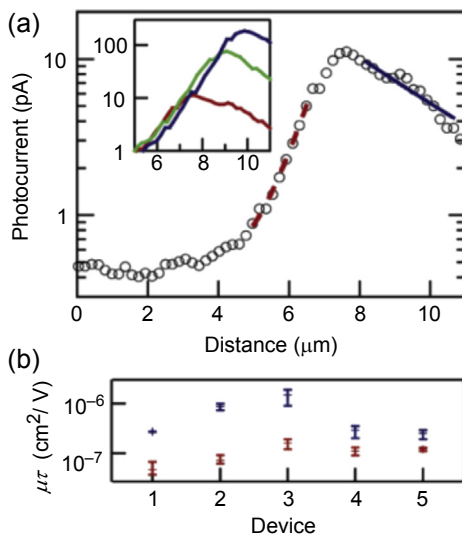


Figure 12.13 Determination of $\mu\tau$ from photocurrent profiles of devices with Ohmic contacts. (a) Photocurrent profile along the NW with the left electrode at 1.0 V bias. The inner edges of the left and right electrodes are at 0 and 11 μm , respectively. The dashed and blue lines are exponential fits to the photocurrent versus distance that determine L_h and L_e , respectively. The slopes do not change appreciably. The units are the same as those in the larger figure. (b) Electron (upper) and hole (lower) values derived from five devices. The error bars correspond to the range of $\mu\tau$ values determined at several applied biases for a given device. Reproduced with permission from [Gu et al. \(2006\)](#). Copyright 2006, American Chemical Society.

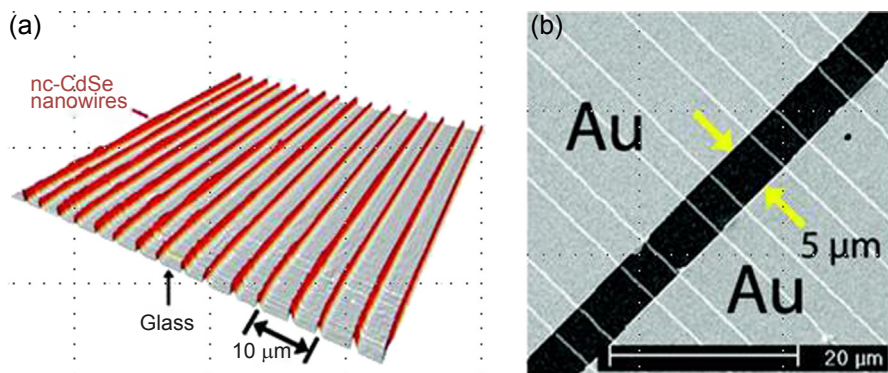


Figure 12.14 (a) Atomic force micrograph of a $80 \times 80\text{-}\mu\text{m}$ area of an array of nc-CdSe nanowires. (b) Scanning electron microscopy images showing the $5\text{-}\mu\text{m}$ gap employed for the photoconductivity measurements of nc-CdSe nanowire arrays; each array contained approximately 350 individual nanowires.

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contact to the nc-CdSe NWs array using 350 NWs in parallel, as shown in Figure 12.14(b).

Current–voltage plots of the arrays, as shown in Figure 12.15(a), were measured under 532-nm -wavelength illumination at 91 mW/cm^2 , from which the photoconductivity can be characterized by photosensitivity of $10\text{--}100$. The response and recovery time, as shown in Figure 12.15(b), which was measured by using the illumination frequency of 3940 Hz , was in the range of $20\text{--}40\text{ }\mu\text{s}$ and is much shorter than that of all the other NW systems. The photoconductive gain G of nc-CdSe NWs was

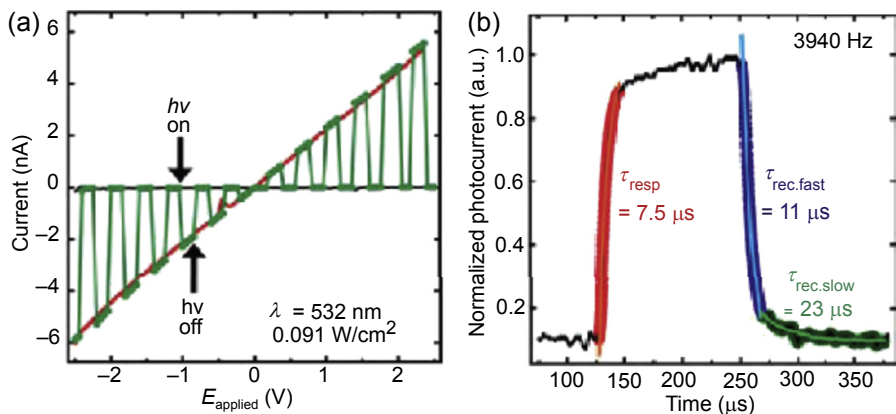


Figure 12.15 (a) Dark current and photocurrent versus applied bias for an array of 350 nc-CdSe nanowires. (b) Photocurrent versus time and the associated time constants for the response and recovery edges.

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estimated to be in the range of 0.032–0.050, quite a bit lower than CdSe films and the other NWs; this is due to the recombination of photogenerated carries at the grain boundary.

Therefore, further study on the mean grain diameter (d_{ave}) dependence of the optoelectronic properties was carried out recently by Kung et al. (2011). Four types of nc-CdSe NWs with different d_{ave} (5, 10, 20, and 100 nm) were prepared by controlling the fabrication process. The power dependence of the photocurrent and the gain characteristics for four nc-CdSe NWs was shown in Figure 12.16. By varying the d_{ave} from 5 to 100 nm, increase in gain and responsivity by a factor of 290 were achieved.

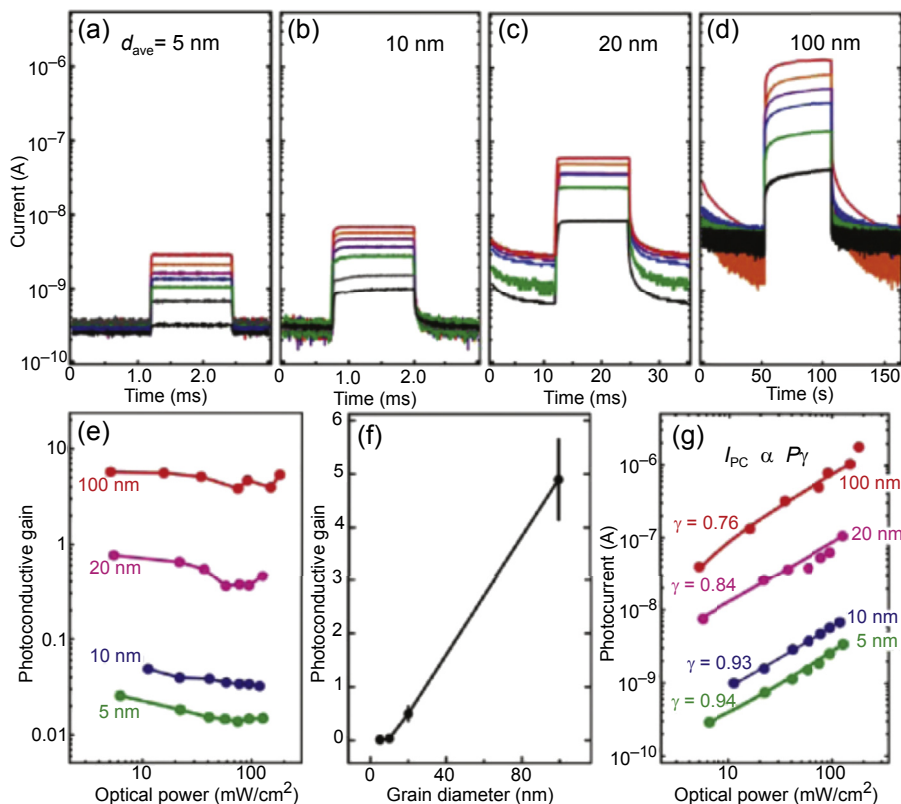


Figure 12.16 (a–d) Optical power dependence of the photocurrent for four nc-CdSe nanowire arrays with d_{ave} as indicated. The ranges of optical powers plotted here are (a) 6.3–128 mW/cm^2 , (b) 11–119 mW/cm^2 , (c) 5.5–95 mW/cm^2 , and (d) 5.5–181 mW/cm^2 . (e) Plot of G versus P optical. In this calculation, it is assumed that 80% of the incident photons are absorbed and that 90% of the 350 nanowires present in each device are electrically continuous. (f) Plot of G versus d_{ave} . (g) Correlation between the generated photocurrent and incident optical power of $350 \times$ nc-CdSe nanowires, plotted as the best fit to a simple power law: $i_{\text{photo}} \propto P^\gamma$ optical. Reproduced with permission from Kung et al. (2011). Copyright 2011, American Chemical Society.

In addition, sensitivity, depending on the incident power, increased by a factor of 375 at $P = 91 \text{ mW/cm}^2$. The increase is attributed to the increase in the mobility-lifetime product with d_{ave} .

12.3.2.3 CdSSe

Composition-graded alloy semiconductor nanostructures on a single substrate are expected as a new material platform used in super broadly tunable nanolasers, color-engineered display and lighting, multispectral detectors, and full-spectrum solar cells (Osellame et al., 2007; Pan et al., 2009; Song et al., 2013). The optoelectronic properties of the $\text{CdS}_{1-x}\text{Se}_x$ alloy NW were investigated by using the structure shown in Figure 12.17(a) (Gu, Yu, Fang, & Tong, 2009), where the composition-graded CdSSe

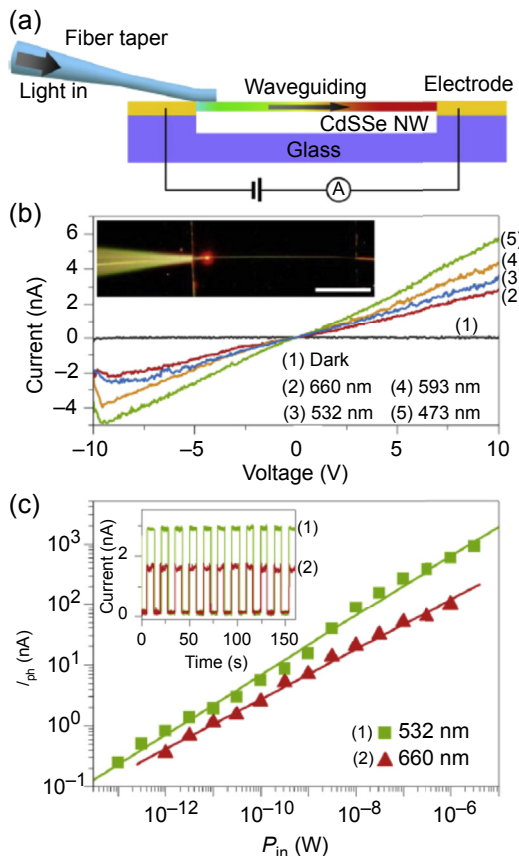


Figure 12.17 (a) Schematic illustration of a CdSSe NW photoconductor. (b) I - V curves of a 350-nm-diameter NW guiding light of different wavelengths with constant $P_{\text{in}} = 100 \text{ pW}$. The black line indicates dark current for reference. Inset, optical micrograph of the CdSSe NW excited by a 660-nm laser. The scale bar is 50 μm . (c) Dependences of the photocurrents of the NW on P_{in} for 532-nm and 660-nm excitation, respectively, and with their reversible responses ($P_{\text{in}} = 30 \text{ pW}$) shown in inset. The NW is biased at 10 V.

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alloy NWs were synthesized by the source-moving thermal evaporation route and the Ohmic contacts were realized by Ti (20 nm)/Au (100 nm) layers.

The typical I – V curves of a 350-nm-diameter CdSSe NW excited by light of different wavelengths with a constant input power (P_{in}) of 100 pW are shown in Figure 12.17(b). These curves show almost linear responses within certain voltage range. The dark current (I_{dark}) of the NW is less than 200 pA at 10 V bias. With input photon energies within the bandgap of the CdSSe NW (grading from 1.74 to 2.44 eV), e.g., 532, 593, and 660 nm in wavelength, significant increases in currents (I_{light}) are obtained by factors ($I_{\text{light}}/I_{\text{dark}}$) of 27, 22, and 15, respectively. However, when the input photon energy is above bandgap (e.g., 473 nm), the response is relatively smaller, as shown in Figure 12.17(b), which is ascribed to the excess carriers generated at the NW surface region due to enhanced absorption.

The power-law dependences of photocurrents on P_{in} at typical wavelengths of 532 and 660 nm are plotted in Figure 12.17(c), from which the large dynamic range and the ultrahigh responsivity at low-level P_{in} can be observed. The time responses of the CdSSe NW are also explored with light on and off for many cycles at $P_{\text{in}} = 30$ pW, as shown in the inset of Figure 12.17(c). The excellent reversibility and stability with rise time of about 100 μs and decay time < 25 ms is illustrated.

12.3.2.4 ZnTe

ZnTe NW, having a direct bandgap of 2.26 eV at 300 K, is a potential material in the optoelectronic nanodevices for pure-green wavelength region, and research on the synthesis and the photoelectric properties of ZnTe NWs has been carried out by several groups (Cao et al., 2011; Huo, Dai, Liu, et al., 2006; Huo, Dai, Xia, et al., 2006; Meng, Jiang, & Mao, 2008; Meng, Jiang, & Mao, 2009; Xie, Zhong, & Basché, 2005; Yong et al., 2007).

S. X. Mao et al. investigated the photoconductivity of ZnTe NWs by using the structure shown in Figure 12.18(a), in which the ZnTe NW with the length of about 10 μm was synthesized by hydrogen-assisted thermal evaporation, the Ni (30 nm)/Au (5 nm) multilayer electrodes were deposited to realize Ohmic contacts, and the four-terminal structure was employed to make the photoconductance less influenced by the contact resistance (Meng et al., 2009). The photoconductivity of individual ZnTe was explored under white light irradiation with different light intensities and was shown in Figure 12.18(b). I – V curve under illumination is linear and the photoconductance G increases by 36.7%, from 3.08 nS in the dark state to 4.21 nS in the light intensity of 36.4 mW/cm². The photogenerated currents at 7 V under different light intensities are given in the inset in Figure 12.18(b) with log–log plot. The photocurrent I_{ph} and the light intensity F can be expressed by a power law, $I_{\text{ph}} \propto F^n$, and the exponent n in this research was fitted to be 0.93, which is in accordance with the theory of carriers provided by Rose.

Photoresponse characteristics of ZnTe NWs were studied by Cao and coworkers by constructing a ZnTe NW-based PD as shown in Figure 12.19, in which the NWs were synthesized by a hydrogen-assisted vapor transport and deposition method

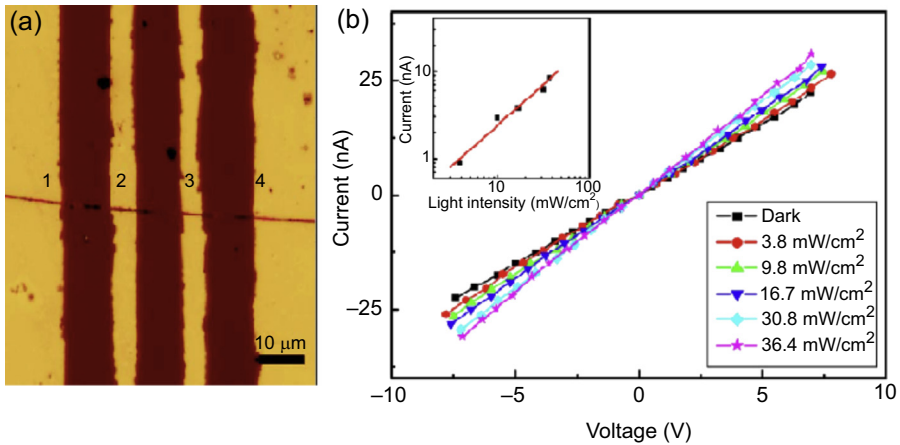


Figure 12.18 (a) Optical image of fabricated four-terminal measurements (bright regions are Ni/Au electrodes) (b) I – V curves of the individual ZnTe nanowire illuminated with light of different intensities.

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(Cao et al., 2011). The ZnTe NW PD also exhibits a relatively fast response of 1.3 s, a good photocurrent reproducibility and stability.

12.3.2.5 ZnO

ZnO NWs have been extensively studied in the past decades for low cost, ease of manufacturing, and their excellent properties in various advanced applications (Guerin, Magne, Pauporté, Le Bahers, & Rathousky, 2010; He, Hsin, Liu, Chen, & Wang, 2007; Kim, Ren, & Jenekhe, 2010; Lupan, Pauporté, & Viana, 2010; Lupan, Ursaki, Chai, Chow, Emelchenko, & Tiginyanu, 2010; Soci et al., 2007; Xiang et al., 2007; Yan, Khoo, Sumboja, & Lee, 2010; Zhang et al., 2009). A wide bandgap ($E_g = 3.37$ eV) structure makes ZnO NWs very suitable for ultraviolet (UV) optoelectronic devices, such as UV radiation monitoring, flame sensing, environment monitoring, and optical communication (Chai, Lupan, Chow, & Heinrich, 2009; Chang, Hsueh, Chen, & Huang, 2008; Chen et al., 2010; Chung et al., 2007; Lupan, Ursaki, et al., 2010; Suehiro et al., 2006). Additionally, it is also found that the surface states on ZnO NW could result in extremely high photoconductive gain, which can be explained by the energy band bending in radial direction of NW. The energy bending prolongs carrier lifetime by separating the photogenerated holes and electrons in the radial direction. This allows developing high sensitive UV PD based on a single ZnO NW. In particular, Soci and coworkers fabricated ZnO NW UV PDs with internal photoconductive gain up to 10^8 (Soci et al., 2007).

However, bandgap modulation along the axial direction is more important, since the majority of NW PDs have been fabricated using single-crystalline NWs. Very recently, a new all-printable method was developed by using polycrystalline ZnO NWs to

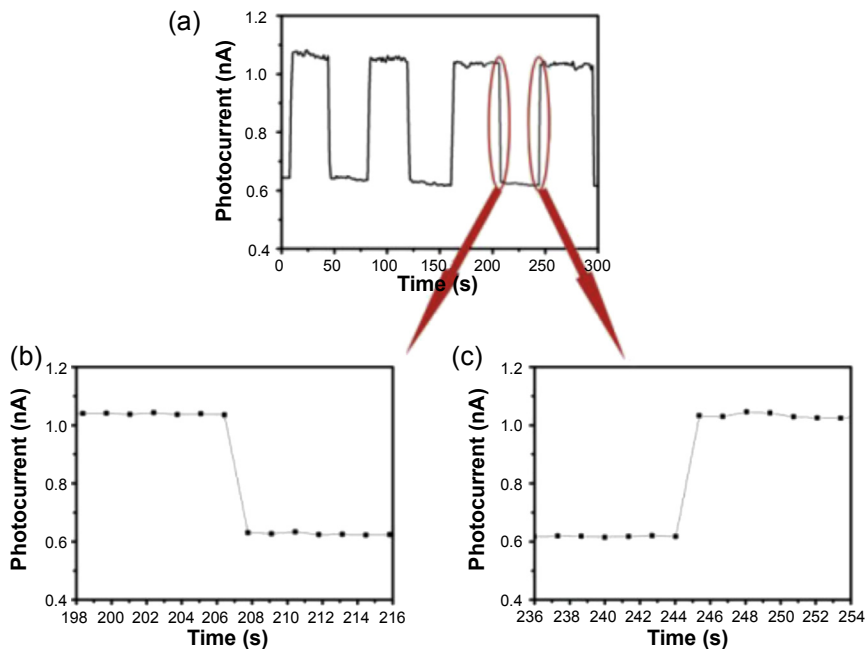


Figure 12.19 (a) The reproducible on/off switching of a ZnTe-nanowire photodetector upon 500-nm light illumination measured for the light-on and light-off conditions at a bias voltage of 10 V. (b, c) The enlarged portions of a 198–216 s range and a 236–254 s range corresponding to light-on to light-off and light-off to light-on transitions, respectively.

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fabricate PDs, which achieved ultrahigh photoconductive gain, responsivity, and detectivity up to 3.3×10^{17} Jones. An all-printed ZnO NWs device shown in [Figure 12.20\(a\)](#) was constructed for detecting UV illumination ([Liu, et al., 2014](#)). The NWs used here were obtained by an electrospinning method. This indicated that the NWs were not single crystalline. Especially, the all-printable method can be used to fabricate devices on flexible substrates, which has great potential future applications. The schematic of the printed PD under UV illumination is shown in [Figure 12.20\(b\)](#). The photoresponse measurement of the PDs was based on this. The performance of a granular NW-based PD with five NWs under UV illumination is summarized. [Figure 12.20\(c\)](#) illustrates the measured current response of the fabricated ZnO granular NWs PD with five NWs under 365-nm UV light illumination with intensity of $77.5 \mu\text{W}/\text{cm}^2$ at bias of 1.0 V. With the light irradiation ON/OFF, the photocurrent of the devices can be readily switched between two distinct states, including a high current state of $6.5 \mu\text{A}$ under UV illumination and a low current state of 20 pA in the dark. [Figure 12.20\(d\)](#) shows I – V characteristics of the PD measured under dark and $0.5 \text{ nW}/\text{cm}^2$, $768.5 \text{ nW}/\text{cm}^2$ and $115.5 \mu\text{W}/\text{cm}^2$. It can be seen that the ON/OFF ratios increase with the illumination intensity increasing,

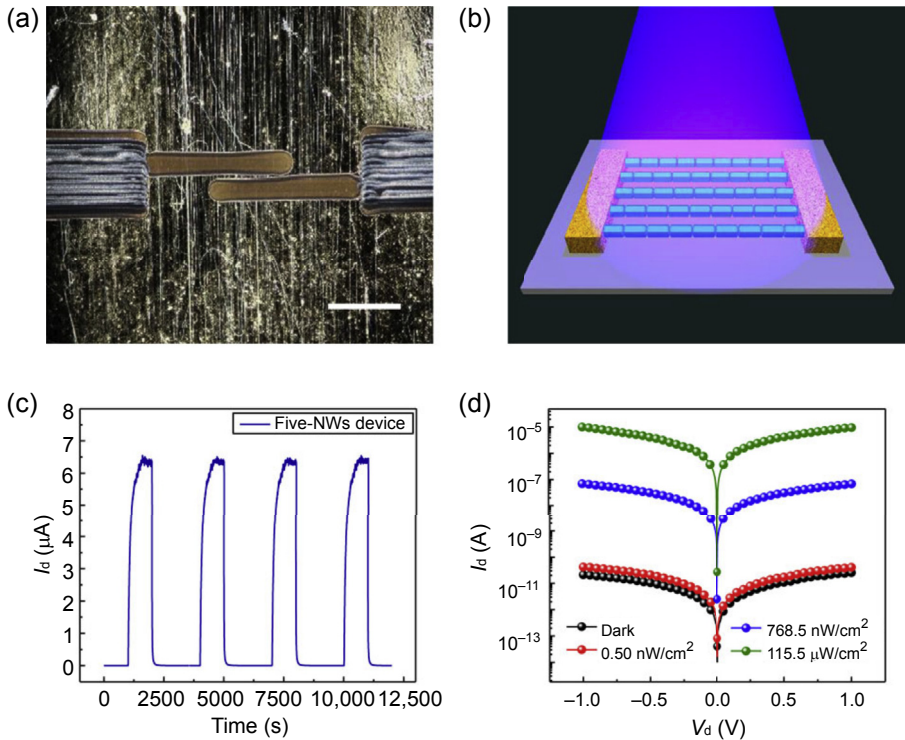


Figure 12.20 ZnO granular NWs photodetectors. (a) An all-printed granular NW photodetector on polyimide substrate. Scale bar, 50 μm . (b) Schematic of a printed ZnO granular NWs photodetector under UV illumination. (c) Repeatable response of a granular NW-based photodetector with five NWs under UV irradiance of $77.5 \mu\text{W}/\text{cm}^2$ at +1 V bias voltage. (d) I – V curves of the printed photodetector under dark, $0.5 \text{ nW}/\text{cm}^2$, $768.5 \text{ nW}/\text{cm}^2$, and $115.5 \mu\text{W}/\text{cm}^2$ of UV illumination at +1 V bias voltage. Reproduced with permission from [Liu et al. \(2014\)](#). Copyright 2014, Nature Publishing Group.

and five orders of magnitude can be achieved for illumination intensities of $\sim 100 \mu\text{W}/\text{cm}^2$ at 1 V bias. This high ratio has not been achieved previously. Z. Y. Fan et al. attributed the high photoconductive gain to the unique band-edge modulation along the granular NW axial direction ([Liu et al., 2014](#)).

12.3.3 Group III–V

12.3.3.1 $\text{InAs}_x\text{P}_{1-x}$

As the two important direct narrow bandgap semiconductors at the IR region, InP and InAs have potential applications in infrared light-emitting and detection devices ([Duan et al., 2001](#); [Liu et al., 2013](#)). The ternary alloys of InP and InAs, $\text{InAs}_x\text{P}_{1-x}$, with the potential bandgap tunability from the near-infrared (for InP ($x = 0$), 1.42 eV) to the

mid-IR region (for InAs ($x = 1$), 0.35 eV), are especially important for realizing broadly tunable IR devices (Thrush *et al.*, 2004).

Based on these $\text{InAs}_x\text{P}_{1-x}$ NWs, wavelength-selective infrared PDs were successfully constructed. For the construction, the as-grown NWs were first dispersed on a $\text{p}^+\text{-Si}$ substrate with SiO_2 (300 nm) layer on top, and then Cr/Au (20 nm/60 nm) electrodes were thermally deposited at the two ends of the wires. The schematic configuration was shown in Figure 12.21(a). Figure 12.21(b)–(f) shows the I – V

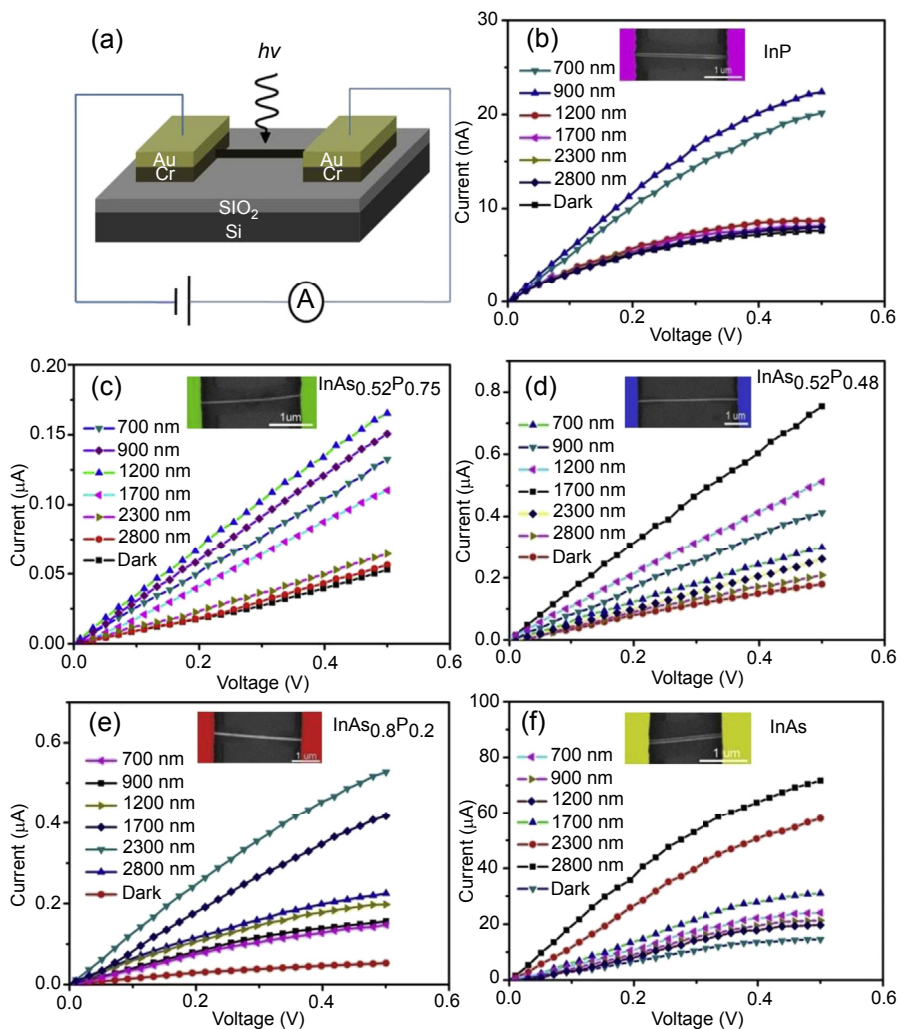


Figure 12.21 (a) Schematic diagram of the NW-based PD testing, (b–f) Representative I – V characteristic for single $\text{InAs}_x\text{P}_{1-x}$ ($x = 0, 0.25, 0.52, 0.8, 1$) NW PDs in dark and under light illumination with different wavelengths ($P_{\text{in}} = 15.3 \text{ mW/cm}^2$) at room temperature. Insets, SEM image of the measured PDs. Reproduced with permission from Ren *et al.* (2014). Copyright 2014, Wiley-VCH.

curves of the achieved detectors based on $\text{InAs}_x\text{P}_{1-x}$ wires with the x value as 0, 0.25, 0.52, 0.80, and 1.0, respectively. The measurements were conducted at room temperature and under the illumination of parallel polarized light (15.3 mW/cm^2) with six typical wavelengths, 700, 900, 1200, 1700, 2300, and 2900 nm, respectively. Insets are the corresponding SEM images of the PDs. The approximate linear shape of the curves reveals good Ohmic contacts between the NWs and the electrodes for all the devices. The results show that the electric conductance of all the devices at dark condition (dark current) are small, but they all increase under the light illumination of different wavelengths. Moreover, the dark currents of ternary $\text{InAs}_x\text{P}_{1-x}$ NWs is higher than the binary compound InP and InAs NWs, which indicates the alloy NWs have higher conductance than the binary ones. In addition, these detectors show different sensitivity to different incident wavelengths. The largest photocurrent for the detectors of NW with $x = 0, 0.25, 0.52, 0.80$, and 1.0 are located at 900, 1200, 1700, 2300, and 2900 nm, respectively.

To obtain the detailed wavelength-related spectral response for these $\text{InAs}_x\text{P}_{1-x}$ NW detectors, the wavelength-dependent photocurrents of the devices were measured with the incident light wavelength scanning from 700 to 3500 nm under an intensity of 15.3 mW/cm^2 and 0.5 V bias, as presented in Figure 12.22(a). It can be seen that the devices with different compositions exhibited different spectral responses. With the composition x value increased from 0 (InP) to 1 (InAs), the peak response wavelength was gradually redshifted from 900 to 2900 nm (seen in Table 1). It is noted that the energy of the peak response wavelengths for all the devices were approached to their corresponding bandgap values of the $\text{InAs}_x\text{P}_{1-x}$ NWs, which was ascribed to the highly efficient generation of electron–hole pairs induced by band-to-band absorption (Pettersson et al., 2006; Tragardh, Persson, Wagner, Hessman, & Samuelson, 2007). Figure 12.22(b) gives the light intensity dependent photocurrents at the peak response wavelength and 0.5 V bias, which showed that all the NW detectors had a very good linear relationship between the illuminated light intensity and photocurrents.

The external quantum efficiency (EQE) of the devices denotes the conversion ability of optical to electrical signals, and is defined as (Gu et al., 1997; Ma et al., 2014)

$$\eta = \frac{I_{\text{ph}}}{q\Phi} = \frac{I_{\text{ph}}}{q} \left(\frac{h\nu}{P_{\text{opt}}} \right) \quad (12.5)$$

where I_{ph} is the photocurrent, $q\Phi$ is the photon flux ($=P_{\text{opt}}/h\nu$), and P_{opt} is the optical power. The corresponding R and EQE values at the peak wavelength of all the devices were calculated and summarized in Table 12.1. From these results, we found the values of R and EQE for ternary $\text{InAs}_x\text{P}_{1-x}$ ($x = 0.8, 0.52, 0.25$) detectors are all higher than those of the binary InP and InAs devices, with the highest values at the composition x of 0.52. It is reported that the electron concentration n of the $\text{InAs}_x\text{P}_{1-x}$ alloys at room temperature will first increase and then decrease when the composition x is increased from 0 to 1, with the highest values appearing at around 0.5 of x value (Bowers, Bauerle, & Cornish, 1959; Kajikawa, Okamura, Inoko, & Mizuki, 2012; Wang & Wessels, 1984). At the same time, the electron mobility μ almost was unchanged for

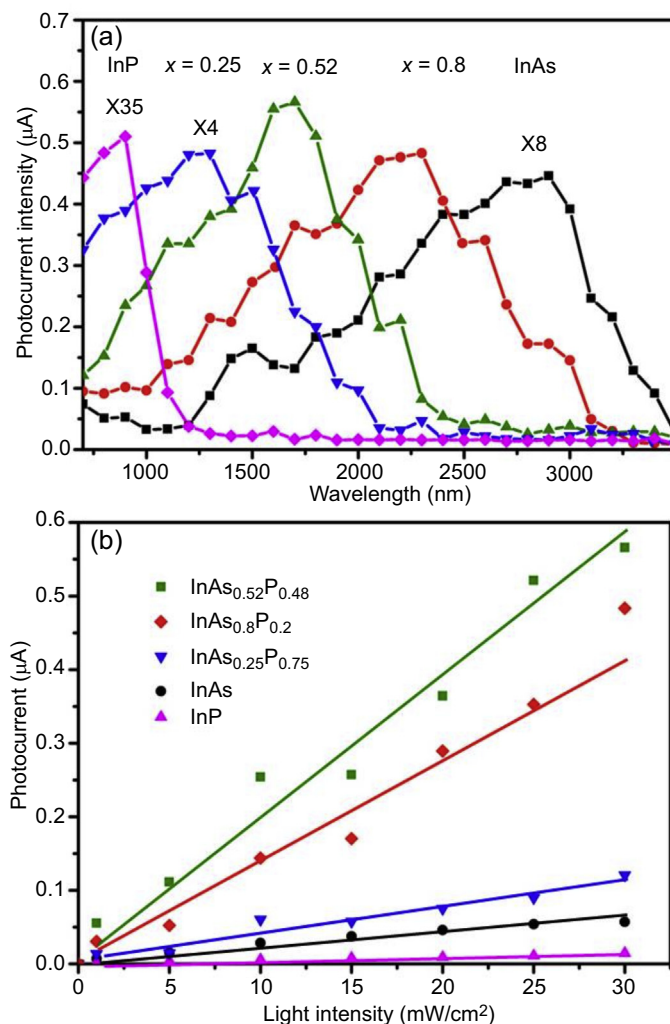


Figure 12.22 (a) The band-dependent photocurrent response of the InAs_xP_{1-x} ($x = 0, 0.25, 0.52, 0.8, 1$) PDs. (b) Photocurrent dependences on the incident power density of InAs_xP_{1-x} at a bias of 0.5 V. Reproduced with permission from Ren et al. (2014). Copyright 2014, Wiley-VCH.

different compositions (x values), because the alloy scattering in InAsP system is not a dominant scattering mechanism at room temperature (Wang & Wessels, 1984). As a consequence, the higher electron density of the ternary NWs than the binary ones induce that the ternary PDs have higher performances (R and EQE) than those of the binary devices, which simultaneously explains that the device with the middle composition ($x = 0.52$) has the best performance.

Table 12.1 Values of R and EQE of photodetectors (PDs) constructed using different composition $\text{InAs}_x\text{P}_{1-x}$ nanowires (NWs)

Sample (x)	E_g (eV)	Peak response wavelength (nm)	R (A/W)	EQE (%)
InAs	0.421 (2945 nm)	2900	1668	7.15×10^4
$\text{InAs}_{0.8}\text{P}_{0.2}$	0.575 (2156 nm)	2300	4998	2.70×10^5
$\text{InAs}_{0.52}\text{P}_{0.48}$	0.828 (1497 nm)	1700	5417	3.96×10^5
$\text{InAs}_{0.25}\text{P}_{0.75}$	1.115 (1113 nm)	1200	3833	3.67×10^3
InP	1.416 (876 nm)	900	337	4.65×10^4

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12.3.3.2 GaSb/GaInSb NW heterostructures

GaSb is an important semiconductor material in the application of infrared PDs because of its narrow direct bandgap (0.725 eV), high hole mobility (850 cm²/Vs) and p-type conducting behavior ([Borg et al., 2010](#); [Dutta, Bhat, & Kumar, 1997](#); [Jeppsson et al., 2008](#)). The bandgap and optoelectronic properties of GaSb can be engineered through In element doping or the formation of GaInSb alloys. It is also reported that $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ alloys with proper In content can bring n-type conducting behavior ([Deng et al., 2012](#); [Rogalski, 1987](#)). The GaSb/GaInSb NW heterostructures were grown using an advanced *in situ* source changing CVD route in a horizontal furnace with a quartz tube. PDs were fabricated using as-grown single GaSb/Ga_{0.9}In_{0.1}Sb NWs. In the fabrication, the NWs were first dispersed on a p-type Si substrate with a 300-nm-thick SiO₂ layer on top. Then two Cr/Au (15 nm/60 nm) electrodes were thermally deposited at the two ends of the NWs. [Figure 12.23](#) shows the I – V curves of a representative NW heterostructure PD, measured in the dark condition and under the illumination of a beam of a monochromatic lights with the wavelength changing from 1100 to 2200 nm (light intensity $P_{\text{in}} = 15.8 \text{ mW/cm}^2$) at room temperature. The I – V curves show that the PDs have clear rectification characteristic, attributed to the formation of a p–n junction within each of these as-grown GaSb/Ga_{0.9}In_{0.1}Sb NW heterostructures. It can be seen that the electric conductance of the devices increased dramatically under the light illumination of all the given wavelengths. The wavelength-dependent photocurrents of the device with the incident light wavelength scanning continuously from 780 to 2250 nm under a bias voltage of 1 V and a light intensity of 15.8 mW/cm² are shown in [Figure 12.24\(a\)](#). It is shown that the PD exhibits dual-band spectral response, with the peaks at 1550

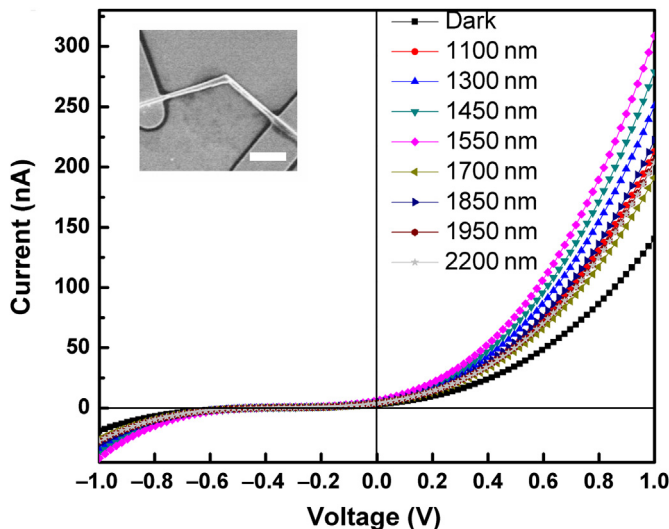


Figure 12.23 I – V curves for a single GaSb/Ga_{0.9}In_{0.1}Sb heterostructure nanowire under light illumination with different wavelengths ($P_{\text{in}} = 15.8 \text{ mW/cm}^2$) at room temperature. Inset, SEM image of the measured photodetector. The scale bar is $2 \mu\text{m}$.

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and 1950 nm, which corresponded to the band-to-band charge generation processes of the GaSb and Ga_{0.9}In_{0.1}Sb materials, respectively. The 1550-nm light response band is significantly stronger than that of the 1950-nm band, and this 1.55- μm light is exactly consistent with the optical communication wavelength because the high energy light ($>0.725 \text{ eV}$, the bandgap of GaSb) can excite simultaneously both segments of the NWs and induce more photogenerated carriers than that of the lower energy light ($<0.725 \text{ eV}$). The EQE of the device at 1550 nm was calculated following [Eqn \(12.5\)](#) to evaluate the conversion ability of optical to electrical signals in the optical communication region (1.55 μm). The result shows that the EQE can reach as high as 8.5×10^4 . [Figure 12.24\(b\)](#) gives the light intensity dependent photocurrent at 1550 nm at a working voltage of 1 V, which demonstrates that the light intensity and the photocurrent have a very good linear relationship. According to the definition of responsivity (R) of a PD and using the photocurrent spectra, the obtained R at 1550 nm for this infrared detector is $1.05 \times 10^3 \text{ A/W}$. [Figure 12.24\(c\)](#) gives the time response of the NW heterostructure PD, which is measured by periodically turning on and off the 1550-nm light at a bias voltage of 1 V. The result indicates that the device exhibits very good reversible switching properties. The response time and recovery time, defined as the time between 10% and 90% of maximum photocurrent, are 2 and 3.7 ms, respectively.

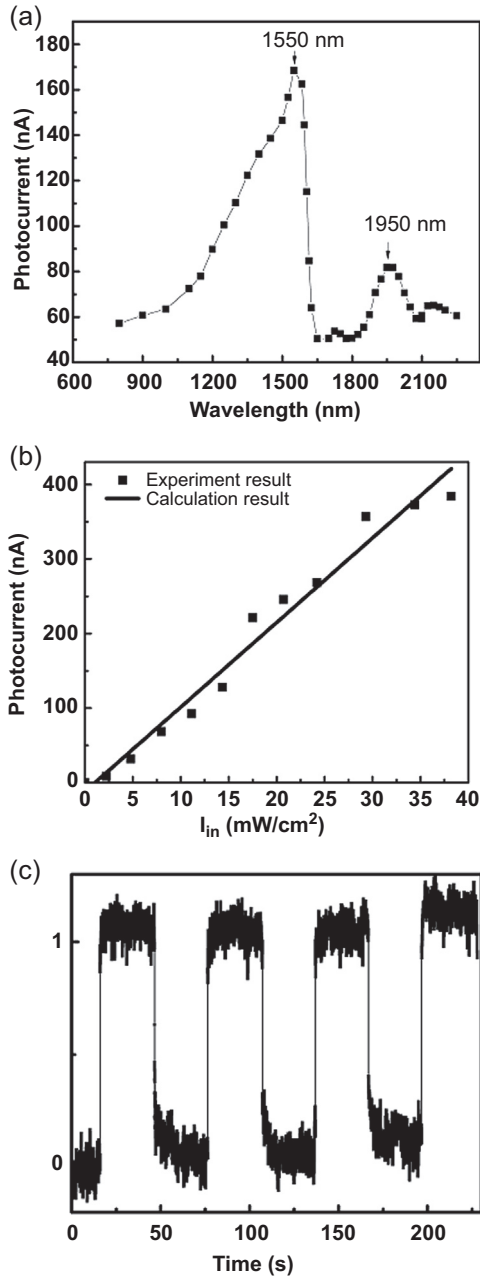


Figure 12.24 (a) The wavelength-dependent photocurrent response of the photodetector. (b, c) The photocurrent dependences on the incident power density and the reproducible on/off switching upon illumination of 1550-nm laser, respectively. Reproduced with permission from [Ma et al. \(2014\)](#). Copyright 2014, American Chemical Society.

12.4 Conclusions

In summary, we have given an overview on the optoelectronic properties of different NW materials, which were extracted from the NW-based photoconductors. Generally, the NWs exhibit high photocurrent gain, due to two factors in the NWs: (1) the prolonged carrier lifetime, which is attributed to the enhanced charge separation due to the surface states; (2) the reduced transit time, which is attributed to the high mobility in the high-quality single-crystal NWs combined with the dramatic shrinking device dimensions. But it should be noted that NWs usually exhibit excellent photo-sensitivity at or near their band edges. For sub-bandgap photons, the decreased response is ascribed to the insufficient absorption in NWs. In the case of photons with energies much larger than the bandgap, the decreased response is ascribed to the excess carriers at the NW surface region induced by the enhanced absorption.

From this overview, we have shown that several useful routes can be employed to fabricate NW-based PDs with enhanced performance: (1) Schottky contact-based devices exhibit higher sensitivity and shorter response time compared to Ohmic contact-based ones, which results from the strong inner electric field at the Schottky contact. (2) Composition and bandgap engineering is an efficient way to realize wide spectral response range due to the extended bandgap region. (3) Rational doping, which introduces energy states within the bandgap, is a successful strategy to tune the band structure and enhance the electrical transport properties of the NWs. (4) Hybrid NWs such as core-shell radial heterojunctions and p-n axial heterojunctions can enlarge the spectra response range due to the integration of materials with different bandgaps, and can facilitate fast carrier separation due to the built-in electric field at the interfaces between the components. It is believed that the introduction of new concepts, such as surface plasmon resonance and the piezophototronic effect, into the design of NW-based PD will bring about interesting results in the future.

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Semiconductor nanowires studied by photocurrent spectroscopy

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13.1 Introduction

First investigations of photocurrents in semiconductor nanowires were performed at the beginning of the millennium (Duan, Huang, Cui, Wang, & Lieber, 2001; Hayden, Agarwal, & Lieber, 2006; Keem et al., 2004; Kind, Yan, Messer, Law, & Yang, 2002). Since then nanowires have been increasingly investigated with respect to future applications in solar cells (Kempa et al., 2008; Tian et al., 2007), photodetectors (Bulgarini et al., 2012; Hayden et al., 2006; Preetel, Padilla, et al., 2012), and optical sensors (Falk et al., 2009; Lee et al., 2004; Lee, Hernandez, Lee, Govorov, & Kotov, 2007). Photocurrent spectroscopy is a powerful tool to identify the generation mechanisms of the photocurrent in nanowire-based devices (Erhard et al., 2013; Preetel, Padilla, et al., 2012). The observed photocurrent effects can be significantly influenced by the nanowire geometry. For instance, the absorption can be dominated by dielectric confinement (Cao et al., 2009; Wang, Gudiksen, Duan, Cui, & Lieber, 2001). Nanowires can be grown with diameters below the Bohr radius, resulting in one-dimensional quantum-confined structures (Law, Goldberger, & Yang, 2004). Furthermore, nanowires with crystal structures not inherent to the bulk have a different band structure and band gap (Maharjan et al., 2009; Trägårdh, Persson, Wagner, Hessman, & Samuelson, 2007). Strain-free heterostructures with radial or axial symmetries make it possible to build new types of optoelectronic nanowire devices, inherently different to circuits based on thin-film technologies (Kuykendall, Ulrich, Aloni, & Yang, 2007; Li & Wang, 2010). Due to the large surface-to-volume ratio, photoconductance effects negligible in bulk semiconductors can further dominate the optoelectronic response of semiconductor nanowires. This chapter is structured as follows: Section 13.2 describes conventional and time-resolved photocurrent spectroscopy. Section 13.3 summarizes the photocurrent and photoconductance effects observed in semiconductor nanowires. Section 13.4 reviews the absorption effects in nanowires investigated by photocurrent spectroscopy. Section 13.5 discusses photocurrent and photoconductance effects for the different nanowire morphologies. The chapter concludes with an outlook in Section 13.6.

13.2 Methods

13.2.1 Conventional photocurrent spectroscopy

Conventional photocurrent spectroscopy explores the photocurrent of electrically contacted semiconductor nanowires as a function of e.g., excitation wavelength, bias voltage, and light polarization. To this end, a laser is focused through an objective onto the nanowire-based circuit and a bias voltage is applied to one of the contacts. In some experiments, a chopper is used to enhance the signal-to-noise ratio (Dunn, 2000) and to get access to optoelectronic processes in the frequency range of Hz to kHz (s to ms).

Up to now, optical absorption experiments on a single nanowire are still challenging and have only been realized for high illumination intensities (Gabriel et al., 2013). Photocurrent spectroscopy, however, enables absorption measurements on single nanowires also for low intensities (Chen et al., 2013), albeit the small fraction of light that is absorbed by a single nanowire (Cao et al., 2009; Kim, Dheeraj, Fimland, & Weman, 2013). In this way, one can get information on the nanowire band structure and joint density of states (Bennett, 1971). Thus, photocurrent spectroscopy can be a good supplement to photoluminescence measurements, as photocurrent spectroscopy can be easily performed at room temperature and it is also applicable to indirect bandgap materials (Chen et al., 2013).

13.2.2 Time-resolved photocurrent spectroscopy

Conventional photocurrent studies are typically limited to timescales exceeding 10 ps (Gallo et al., 2011) because available electronic equipment cannot produce and detect faster trigger signals and transients. Furthermore, optoelectronic charge-carrier dynamics are obscured by the response time of the high-frequency circuits. Yet it is known from optical experiments that carrier relaxation, thermalization, and recombination processes can occur on much faster timescales in semiconductor nanowires (Johnson et al., 2004). Using time-resolved photocurrent spectroscopy, one can investigate the dynamics of photo-thermoelectric currents and displacement currents, the transport of photogenerated charge carriers to the electrical contacts, and the photo-Dember effect, as well as the carrier lifetime-limited currents with a picosecond time-resolution (Figure 13.1). In time-resolved measurements, the individual current contributions can be separated because of their characteristic timescales and dynamics in nanowires. Moreover, the drift velocity of the photogenerated holes can be explored (Erhard et al., 2013; Prechtel, Padilla, et al., 2012). The results obtained by time-resolved photocurrent spectroscopy prove useful for the design of nanowire-based photodetectors, photoswitches, solar cells, and high-speed transistors.

Two major pump–probe methods exist to measure the time-resolved photocurrent on a picosecond timescale. These are photocurrent autocorrelation spectroscopy (Erhard et al., 2013; Gabor, Zhong, Bosnick, & McEuen, 2012; Urich, Unterrainer, & Mueller, 2011) and THz time-domain photocurrent spectroscopy (Erhard et al., 2013; Prechtel, Padilla, et al., 2012).

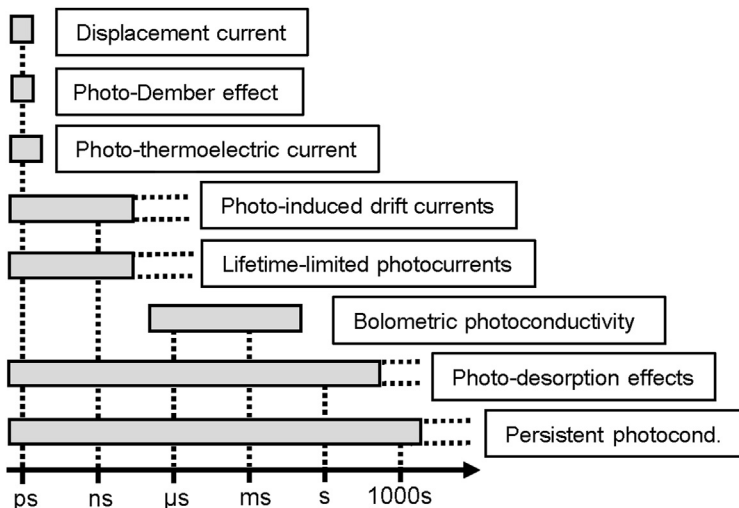


Figure 13.1 Characteristic timescales of photocurrent and photoconductance phenomena in semiconductor nanowires ranging from picoseconds to 1000s of seconds.

13.2.2.1 Photocurrent autocorrelation spectroscopy

For photocurrent autocorrelation spectroscopy, a pump laser pulse is focused on the nanowire (Figure 13.2). This exciting pulse needs to be intense enough to generate a photocurrent in saturation (e.g., because of bleaching due to state filling (Ahn et al., 2012; Li et al., 2014; Lo et al., 2012)). A second probe laser pulse hits the

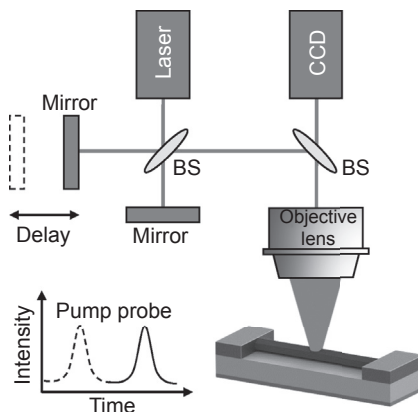


Figure 13.2 Experimental setup to measure the photocurrent autocorrelation. A laser beam with laser pulses in the femtosecond regime is split into a pump and a probe pulse and they are subsequently recombined by a beam splitter (BS) (Erhard et al., 2013; Gabor et al., 2012; Urich et al., 2011). The time delay between the pump and the probe pulse is adjusted by a translation stage in one of the two beam paths. Both laser beams are focused onto the electrically contacted nanowire, and the photocurrent is measured as a function of the time delay.

nanowire at the same position after a time delay Δt . The probe laser pulse can only excite additional charge carriers and hereby an additional photocurrent if the saturation photocurrent induced by the pump laser pulse is already partially relaxed after Δt . Hereby, photocurrent relaxation times in the picosecond regime have been explored (Erhard et al., 2013). However, photocurrent effects that do not saturate such as the photo-thermoelectric effect (Section 13.3.2) cannot be explored by photocurrent autocorrelation spectroscopy.

13.2.2.2 THz time-domain photocurrent spectroscopy

Another possibility to measure the photocurrent of a nanowire with a picosecond time-resolution is the so-called THz time-domain photocurrent spectroscopy (Erhard et al., 2013; Prechtel, Padilla, et al., 2012). Compared to photocurrent autocorrelation spectroscopy, it also works in the nonsaturation regime, because the time-resolution is achieved by the utilization of an Auston switch (Figure 13.3). First, the electrically contacted nanowire is excited by a femtosecond laser pump pulse. The photogenerated currents in the nanowire induce an electromagnetic transient in the strip lines, by which the nanowire is contacted (optical microscope image in Figure 13.3). The transient is directly proportional to the photocurrent, and it propagates along the strip lines to the field probe where the so-called Auston switch is excited by a probe laser pulse at a time delay Δt . The Auston switch is a silicon photo-switch with a subpicosecond response time (Auston, 1983; Doany, Grischkowsky, & Chi, 1987). If at the time delay the electromagnetic transient is present at the Auston switch, the photogenerated charge carriers in the silicon amount to a current I_{sampling} in the field probe. Hereby, the photocurrent of the nanowire can be sampled as a function of Δt with a picosecond time-resolution (Erhard et al., 2013, 2015; Prechtel, Padilla, et al., 2012). The THz-time-domain photocurrent spectroscopy makes it possible to characterize nanowires in an all-encompassing way as conventional photocurrent spectroscopy but with a time-resolution of picoseconds (Prechtel et al., 2011; Prechtel, Song, et al., 2012).

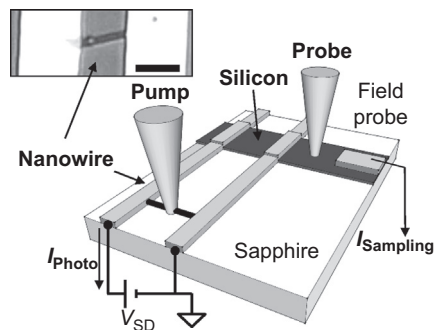


Figure 13.3 Experimental setup for a THz time-domain photocurrent spectroscopy on a single semiconductor nanowire. Inset: optical microscope image of an InAs nanowire. Scale bar 4 μm . See text for further information (Erhard et al., 2013).

In particular, THz time-domain spectroscopy can be used to explore photo-thermoelectric effects, displacement and drift currents (photovoltaic effects), recombination processes, and THz oscillations in single nanowires (Erhard et al., 2013; Prechtel, Padilla, et al., 2012).

13.3 Photocurrent dynamics in semiconductor nanowires

In principle, photocurrents involve two main physical processes: optical absorption and charge transport (Chen et al., 2011; Chen et al., 2013; Sze & Ng, 2007). However, one can distinguish several optoelectronic dynamics with different timescales (Figure 13.1), as will be discussed in the following sections.

13.3.1 Photovoltaic effects

In a naïve picture, the photovoltaic effect is the generation of a voltage when a device is exposed to light (Sze & Ng, 2007). To achieve this in a nanowire-based device, an intrinsic electric field, for example, due to a space charge region, has to be present. In turn, a photocurrent is generated along the forward direction of the space charge region (Kittel, 1995). In literature, the photovoltaic effect in nanowires has been investigated for a broad variety of cases, as will now be discussed.

At a metal-semiconductor interface, a space-charge region may occur (Sze & Ng, 2007). By illuminating this Schottky contact, a photocurrent is generated. This photovoltaic effect has been observed for many different nanowires made of CdS (Gu et al., 2005), GaAs (Thunich et al., 2009), GaN (Deb et al., 2006), Ge (Kim, Lee, Cho, Kang, & Jo, 2010), Si (Ahn, Dunning, & Park, 2005), and ZnO (Heo et al., 2004; Keem et al., 2004) contacted by metals such as Au (Keem et al., 2004; Thunich et al., 2009), Ni (Ahn et al., 2005), Pt (Deb et al., 2006; Heo et al., 2004), and Ti (Gu et al., 2005). In addition, at the interface between a semiconductor nanowire and a zero bandgap material, such as graphene, a photovoltaic effect can be observed and the results can be equally explained in terms of a Schottky barrier (Dufaux, Boettcher, Burghard, & Kern, 2010; Fan et al., 2011).

Bulk photovoltaic devices typically consist of a pn homojunction or heterojunction (Sze & Ng, 2007). This concept was also realized in semiconductor nanowires (Garnett, Brongersma, Cui, & McGehee, 2011; Peng & Lee, 2011). Due to the nanowire geometry, however, there exist several possibilities to implement such junctions in a nanowire device (Figure 13.4). One way to achieve a nanowire pn junction is to deposit a p-type nanowire on a crossing n-type nanowire (Figure 13.4(a)) (Cui, 2001; Duan et al., 2001; Hayden et al., 2006). Further possibilities are photovoltaic devices made out of radial (Figure 13.4(b)) (Christesen et al., 2012; Czaban, Thompson, & LaPierre, 2009; Dong, Tian, Kempa, & Lieber, 2009; Garnett & Yang, 2008; Krogstrup et al., 2013; Mariani et al., 2011; Tang, Huo, Brittman, Gao, & Yang, 2011; Tian et al., 2007; Wang, Wang, Yip, Fitzgerald, & Antoniadis, 2010) or axial (Figure 13.4(c))

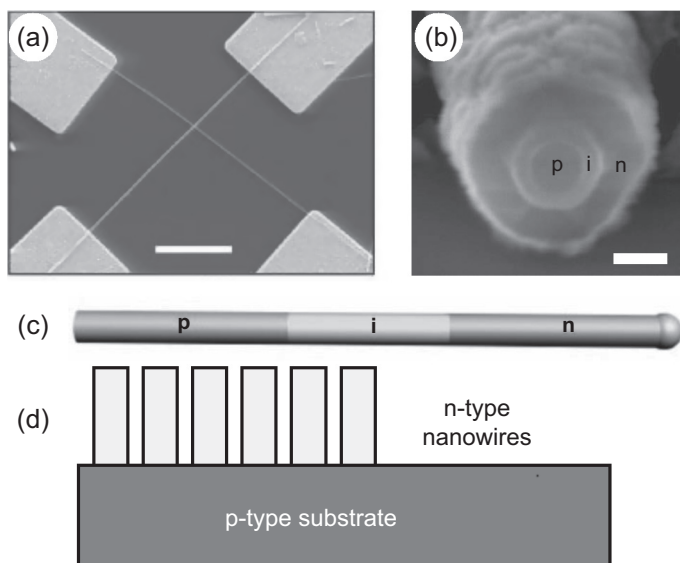


Figure 13.4 Nanowire geometries for homo- and heterojunctions. (a) Scanning electron microscope (SEM) image of a p-doped InP nanowire crossing an n-doped InP nanowire. Scale bar 2 μm . (Reprinted by permission from Macmillan Publishers Ltd: *Nature* (Duan et al., 2001), copyright 2001.) (b) SEM image of a radial p(i)n-junction within a nanowire. Scale bar 100 nm. (Reprinted by permission from Macmillan Publishers Ltd: *Nature* (Tian et al., 2007), copyright 2007.) (c) Schematic illustration of an axial p(i)n-junction nanowire. (Reprinted with permission from (Kempa et al., 2008). Copyright 2008 American Chemical Society.) (d) Schematic illustration of a nanowire-substrate junction.

(Christesen et al., 2012; Guo et al., 2010; Heurlin et al., 2011; Kempa et al., 2008; Li et al., 2009; Lin et al., 2011; Reimer, 2011; Sivakov et al., 2009) pn junctions within the nanowires. Moreover, p-doped (n-doped) substrates with n-doped (p-doped) nanowires grown on top can also exhibit a photovoltaic effect (Figure 13.4(d)) (Garnett & Yang, 2010; Peng et al., 2005; Stelzner et al., 2008; Tang et al., 2008; Wei et al., 2009). For n-type ZnO nanowires combined with p-type CdSe (Leschkes et al., 2007) or CuO₂ (Yuhua & Yang, 2009) nanoparticles, photovoltaic effects have been reported. Moreover, solar cells have also been built by embedding an n-type nanowire array in a thin film of a p-type semiconductor (Bie et al., 2010; Fan et al., 2009; Lévy-Clément, Tena-Zaera, Ryan, Katty, & Hodes, 2005).

Last but not least, bending a nanowire induces mechanical strain, which causes internal electric fields, thereby separating photogenerated electrons and holes (Greil, Bimer, Bertagnoli, & Lugstein, 2014; Wu, Neaton, & Grossman, 2009). Such a strain-induced photovoltaic effect was observed in Ge nanowires (Greil et al., 2014).

The photovoltaic effect can generate photocurrents on different timescales. On short timescales, in the first picoseconds after a pulsed laser excitation, the generation of additional charge carriers may cause a displacement current by which electric fields are screened. On timescales of picoseconds up to nanoseconds, the photocurrents

can be dominated by the drift current of slow photogenerated charge carriers, such as holes, and the carrier lifetime-limited current (Erhard et al., 2013; Prechtel, Padilla, et al., 2012). All of these currents are related to electric fields within a nanowire.

13.3.2 Photo-thermoelectric effect

The photo-thermoelectric effect is due to a local increase of the electron temperature induced by the laser illumination (Fu et al., 2011). A temperature difference ΔT at the interface of a nanowire and a second material, for example, a metal contact, may result in a thermoelectric current:

$$I_{\text{Thermo}} = (S_{\text{nanowire}} - S_{\text{contact}})\Delta T/R,$$

with the Seebeck coefficients of the nanowire S_{nanowire} and the metal contact S_{contact} and R the total resistance of the electrical circuit (Fu et al., 2011; Prechtel, Padilla, et al., 2012; Varghese, Tamang, Tok, Mhaisalkar, & Sow, 2010). So far, the photo-thermoelectric effect has been observed in GaAs- (Prechtel, Padilla, et al., 2012), InAs- (Erhard et al., 2013), and VO₂-based (Varghese et al., 2010) nanowires with typical relaxation times below 10 ps (Erhard et al., 2013; Prechtel, Padilla, et al., 2012). The contribution of the photo-thermoelectric current to the total photocurrent is often negligible, because the typical laser illumination intensities for photocurrent measurements raise the local temperature only by one-tenths to a few Kelvin, and typical Seebeck coefficients are of the order $\mu\text{V/K}$ (Ahn et al., 2005; Fu et al., 2011). The photo-thermoelectric effect must not be confused with the bolometric effect (see Section 13.3.3.4).

13.3.3 Photoconductance effects

As nanowires have a large surface-to-volume ratio, they are very sensitive to surface effects, such as the Fermi-level pinning leading to an accumulation or depletion layer at the nanowire surface (Hasegawa & Grey, 2002). The latter may induce a photoconductive gain (Ahmad, Rasool, Rafiq, & Hasan, 2012; Ahn & Park, 2007; Calarco et al., 2005; Chen et al., 2011; González-Posada, Songmuang, Den Hertog, & Monroy, 2012; Hof et al., 2008; Kim et al., 2010; Polenta et al., 2008; Rossler et al., 2008; Sanford et al., 2010; Thunich et al., 2009; Zhai et al., 2010), a photodesorption effect (Calarco, Stoica, Brandt, & Geelhaar, 2011; Harnack, Pacholski, Weller, Yasuda, & Wessels, 2003; den Hertog et al., 2012; Hsu et al., 2005; Huang & Zhang, 2010; Hullavarad, Hullavarad, Look, & Claflin, 2009; Kind et al., 2002; Li, Gao, Wang, & Wang, 2005; Pfüller et al., 2010; Prades et al., 2008; Soci et al., 2007; Suehiro et al., 2006), or even a persistent photoconductance (Ahmad et al., 2012; Calarco et al., 2005; Chen et al., 2011; González-Posada et al., 2012; Polenta et al., 2008; Rasool, Rafiq, Ahmad, Imran, & Hasan, 2012; Sanford et al., 2010; Winkelmann et al., 2007; Zhai et al., 2010). Furthermore, the temperature dependence of the conductivity may lead to a bolometric photoconductance effect (Tilke, Pescini, Lorenz, & Blick, 2003).

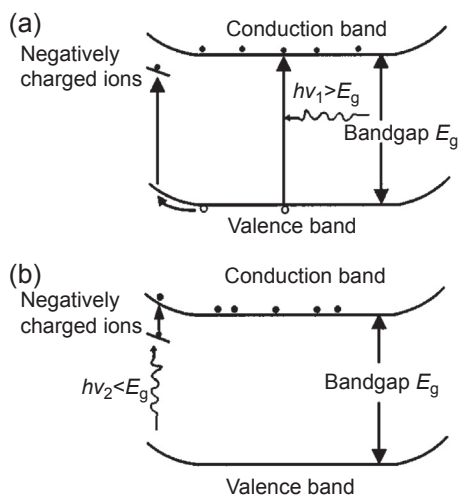
13.3.3.1 Photoconductive gain effect

As atoms at the crystal surface lack neighbors, surface reconstruction or adsorption of foreign atoms (see Section 13.3.3.2) may occur. New states are thereby formed at the surface, which can lead to a Fermi-level pinning and a surface band bending (Ashcroft & Mermin, 1987; Hasegawa & Grey, 2002; Spicer, Chye, Garner, Lindau, & Pianetta, 1979). The intrinsic electric field of the surface band bending points perpendicular to the nanowire axis. However, it can contribute twofold to the photoresponse of nanowires: (1) for an upbending (downbending) at the surface, photogenerated holes (Rossler et al., 2008) (electrons) (Kim et al., 2010; Thunich et al., 2009) are trapped at the surface, acting as a positive (negative) gate charge. In turn, the conducting part of the nanowire is increased (Thunich et al., 2009). This effect is sometimes called the photogating effect. (2) The photogenerated electrons (Ahmad et al., 2012; Ahn et al., 2007; Calarco et al., 2005; Rossler et al., 2008) (holes) (Kim et al., 2010; Thunich et al., 2009) increase the density of free charge carriers in the nanowire core, which is called the photodoping effect. The photogating effect was reported for GaAs- (Rossler et al., 2008; Thunich et al., 2009) and Ge-based (Kim et al., 2010) nanowires, and the photodoping effect for GaAs- (Rossler et al., 2008; Thunich et al., 2009), Ge- (Ahn et al., 2007; Kim et al., 2010), GaN- (Calarco et al., 2005; Chen et al., 2011; González-Posada et al., 2012; Polenta et al., 2008; Sanford et al., 2010), InSe- (Zhai et al., 2010), and Si-based (Ahmad et al., 2012) nanowires. However, photogating and photodoping are interconnected to each other, because an interband excitation always generates electrons and holes in the nanowire.

13.3.3.2 Photodesorption effect

Photodesorption of chemisorbed or physisorbed foreign atoms can influence the conductivity of a nanowire as well (Figure 13.5). This photoconductance effect was observed in n-type semiconductor nanowires for chemisorbed oxygen

Figure 13.5 Schematic energy band diagram illustrating the photodesorption effect for illumination with photons having an energy (a) higher and (b) lower than the bandgap energy. The band bending upwards at the nanowire surface is due to oxygen adsorption (negatively charged ions). Reprinted with permission from Li et al. (2005). Copyright 2005, AIP Publishing LLC.



(Harnack et al., 2003; Hsu et al., 2005; Hullavarad et al., 2009; Keem et al., 2004; Kind et al., 2002; Lee et al., 2004; Li et al., 2005; Prades et al., 2008; Suehiro et al., 2006; Yoon et al., 2010). In the dark, oxygen adsorbs at the nanowire surface by capturing free electrons: $\text{O}_2(\text{g}) + \text{e}^- \rightarrow \text{O}_2^-(\text{ad})$ (Kind et al., 2002; Melnick, 1957), which creates a bend bending upwards near the nanowire surface. In turn, a depletion layer is formed with low conductivity (Kind et al., 2002; Li et al., 2005; Soci et al., 2007). Exposing the nanowire to light may lead to photogenerated holes, which migrate to the surface and discharge the adsorbed oxygen: $\text{O}_2^-(\text{ad}) + \text{h}^+ \rightarrow \text{O}_2(\text{g})$ (Kind et al., 2002; Melnick, 1957) (Figure 13.5(a)).

In the literature two processes are reported. (1) For photons with an energy higher than the bandgap of the nanowire, the remaining photogenerated electrons increase the conductivity of the nanowire core (Figure 13.5(a)) (Harnack et al., 2003; Hsu et al., 2005; Keem et al., 2004; Kind et al., 2002; Lee et al., 2004; Li et al., 2005; Soci et al., 2007; Yoon et al., 2010). The increased electron density may also reduce the width and height of Schottky barriers (Keem et al., 2004). (2) For photons with an energy smaller than the bandgap of the nanowire, electrons trapped at defect states related to the adsorbed oxygen are photoexcited to the conduction band. Hereby, the density of free charge carriers increases and the potential barriers are reduced (Figure 13.5(b)) (Keem et al., 2004; Li et al., 2005).

The photodesorption effect of oxygen has been shown for ZnO (Harnack et al., 2003; Hsu et al., 2005; Hullavarad et al., 2009; Kind et al., 2002; Li et al., 2005; Prades et al., 2008; Soci et al., 2007; Suehiro et al., 2006), SnO_2 (Lee et al., 2004), CdSe (Yoon et al., 2010), ZnSe (Yoon et al., 2010), WO_3 (Huang & Zhang, 2010), and GaN nanowires (Calarco et al., 2011; den Hertog et al., 2012; Pfüller et al., 2010). In p-type ferroelectric semiconductor nanowires of SbSI, a negative photoconductive effect due to water desorption was found (Nowak et al., 2014).

13.3.3.3 Persistent photoconductance effects

Persistent photoconductivity describes a class of transport phenomena that prevail on a timescale of seconds to hours. There are several processes being classified as persistent photoconductivity in literature.

1. Surface band bending leads to a spatial separation of photogenerated holes and electrons (see Section 13.3.1) and in turn to a reduced recombination rate (Ahmad et al., 2012; Calarco et al., 2005; Chen et al., 2007; Chen et al., 2011; González-Posada et al., 2012; Polenta et al., 2008; Sanford et al., 2010). This effect sensitively depends on the nanowire diameter (Calarco et al., 2005; Chen et al., 2011; González-Posada et al., 2012; Polenta et al., 2008), and it has been observed for GaN (Calarco et al., 2005; Chen et al., 2011; González-Posada et al., 2012; Polenta et al., 2008; Sanford et al., 2010), InSe (Zhai et al., 2010), and Si (Ahmad et al., 2012; Rasool et al., 2012; Winkelmann et al., 2007) nanowires.
2. Both adsorption and desorption of molecules on a surface of the nanowire (see Section 13.3.2) are rather slow processes. The increase and decrease of the photoconductivity can occur on a timescale of seconds to hours depending on ambient gas conditions and materials (Harnack et al., 2003; Hsu et al., 2005; Hullavarad et al., 2009; Keem et al., 2004; Kind et al., 2002; Nowak et al., 2014; Prades et al., 2008; Soci et al., 2007; Suehiro et al., 2006; Yoon et al., 2010).

3. Defect states in the nanowire core may also lead to a persistent photoconductivity. For ZnO nanowires, such a phenomenon was explained by oxygen vacancy states that were excited to a metastable charged state (Hullavarad et al., 2009; Lany & Zunger, 2005; Prades et al., 2008; Wang et al., 2011). An equivalent effect was reported for other II–VI and chalcopyrite Cu–III–VI₂ semiconductors with anion vacancy states (Lany & Zunger, 2005). In GaAs/AlGaAs nanowires with a Si delta-doping, deep DX centers can freeze out while capturing electrons at low temperatures (4.2 K), and the captured electrons can be activated via illumination, leading again to a persistent photoconductance (Spirkoska, Fontcuberta i Morral, Dufouleur, Xie, & Abstreiter, 2011).

13.3.3.4 Bolometric photoconductivity

The conductivity σ of a semiconductor is a function of temperature (Sze & Ng, 2007). With absorption of photons, hot electrons are generated, which redistribute their energy via electron–electron scattering processes on a femtosecond to picosecond timescale in the electron bath (Elsaesser & Shah, 1991; Neppi, Kotthaus, & Koch, 1979). This leads to an increased electron temperature T_{el} relative to the lattice temperature T_{lat} as the direct relaxation via phonon emission is less efficient (Neppi et al., 1979). There are three features characteristic for bolometric photoconductivity. (1) The bolometric effect can be enhanced if the thermal coupling to the environment is reduced (Henini & Razeghi, 2002; Neppi et al., 1979). (2) Typical relaxation times from 1 μs (Neppi et al., 1979) to 100 ms (Henini & Razeghi, 2002; Itkis, 2006) are reported. (3) The magnitude of the bolometric photoconductivity depends on the temperature derivative of the conductivity (Henini & Razeghi, 2002; Itkis, 2006). The bolometric effect was observed for a suspended Si nanowire in the Coulomb blockade regime (Tilke et al., 2003).

13.4 Absorption effects in semiconductor nanowires

By measuring the photocurrent, one can get information about absorption effects in single nanowires. Krogstrup et al. showed that the absorption of a single-standing nanowire is enhanced due to its light-concentrating property (cf. Figure 13.6) (Krogstrup et al., 2013), whereas a single Si nanowire with a diameter of 900 nm lying on a substrate can exhibit a partially coherent thin film absorption spectrum (Kelzenberg et al., 2008). Thinner Ge nanowires (10–110 nm) lying on a substrate have absorption peaks due to leaky mode resonances, which is consistent with Lorenz–Mie theory for light scattering (Cao et al., 2009).

Because of the elongated geometry of nanowires, their absorption depends on the polarization of the exciting photons described by the polarization anisotropy $\rho = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, with $I_{\parallel}$ ($I_{\perp}$) the photocurrent for parallel (perpendicular) polarized light to the nanowire. ρ is generally positive for semiconductor nanowires, as polarized light parallel to the nanowire can be better absorbed than perpendicularly polarized light. This can be explained by the dielectric mismatch of the vacuum and the nanowire material (Cao et al., 2009; Wang et al., 2001). When the wavelength λ of the exciting light gets into the range of the nanowire

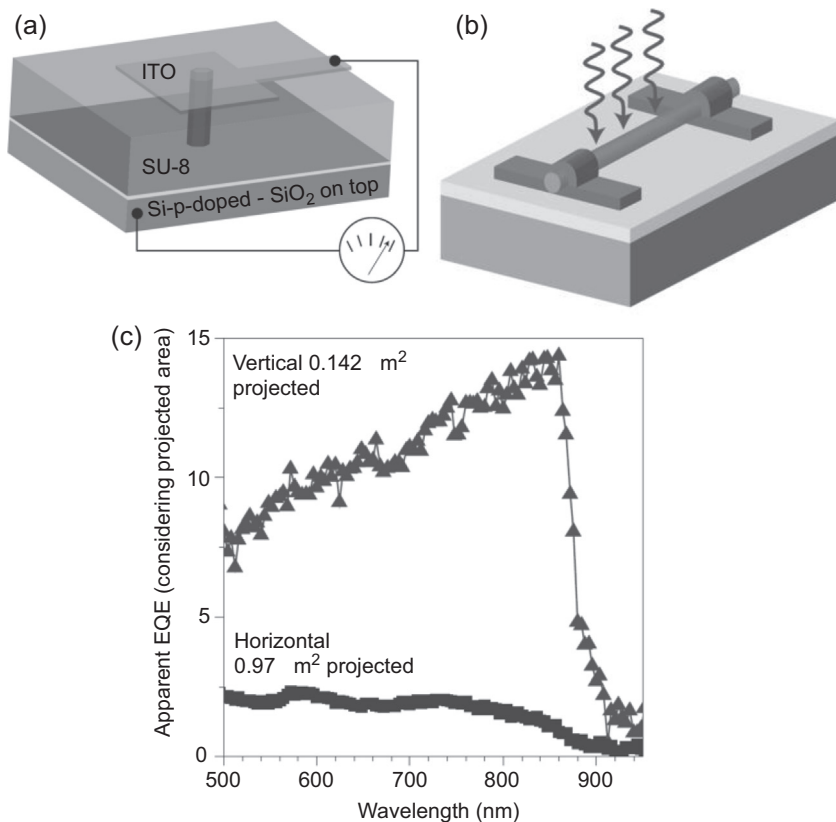


Figure 13.6 Schematic illustration of the device geometry to measure the photocurrent of a single nanowire (a) standing and (b) lying on an SiO_x/Si substrate. (c) The external quantum efficiency (EQE) for a lying nanowire (horizontal) and a standing nanowire (vertical). (a) and (c) reprinted by permission from Macmillan Publishers Ltd: *Nature Photonics* (Krogstrup et al. (2013)), copyright 2013. (b) reprinted by permission from Macmillan Publishers Ltd: *Nature Materials* (Cao et al. (2009)), copyright 2009.

diameter $d \approx \lambda/n_{\text{NW}}$, the effect vanishes (Persano et al., 2011) (n_{NW} is the refractive index of the nanowire). The polarization anisotropy can also influence the all-optical quantum interference control of electrical currents in single GaAs nanowires (Ruppert et al., 2010).

In addition, Fano resonances in Si nanostripe photodetectors have been investigated by measuring the scattering spectra (by bright- and dark-field microscopy) and the absorption spectra (by photocurrent spectroscopy). Fan et al. found that the Fano resonance and by this the absorption resonance can be tuned by the nanostripe width (Fan, Yu, Fan, & Brongersma, 2014).

Moreover, the recombination time of photogenerated charge carriers in a nanowire can be extracted from time-resolved photocurrent spectroscopy. In p-doped GaAs nanowires, a recombination time of 1.5 ns was observed by THz time-domain

photocurrent spectroscopy (Prechtel, Padilla, et al., 2012). This value is smaller than the 2.5 ns found by photoluminescence measurements (Demichel, Heiss, Bleuse, & Mariette, 2010), as the recombination dynamics in photocurrent measurements are modified by the charge transport to the metal contacts (Prechtel, Padilla, et al., 2012).

13.5 Morphologies explored by photocurrent spectroscopy

13.5.1 Crystal structures

Photocurrent spectroscopy can be used to investigate the band structure of a single semiconductor nanowire (Chen et al., 2013). Using this technique, the bandgaps of several types of nanowires have been characterized. InP zinc-blende nanowires exhibit a bandgap energy about 70 meV larger than wurtzite nanowires at room temperature (Maharjan et al., 2009). P-doped GaAs nanowires have a room temperature bandgap of about 1.42 eV (Thunich et al., 2009). The bandgap of wurtzite $\text{InAs}_{1-x}\text{P}_x$ nanowires for different P contents has been measured by photocurrent spectroscopy, showing that wurtzite InAs (InP) has a bandgap of 0.54 eV (1.65 eV) at 5 K (Trägårdh et al., 2007).

13.5.2 Surfaces and interfaces

Photocurrents make it possible to probe local electric fields in the nanowires and thereby the surfaces and interfaces. For instance, surface band bending caused by Fermi-level pinning at the semiconductor surface (Sze & Ng, 2007) can lead to a Franz Keldysh effect (Franz, 1958; Keldysh, 1958) and by this to a subband gap absorption and photocurrent (cf. Figure 13.7). This effect is prominent for nanowires due to their large surface-to-volume ratio, and it has been found for GaN- (Cavallini et al., 2007) and GaAs-based (Thunich et al., 2009) nanowires. Furthermore, photocurrent spectroscopy was used to investigate the homogeneity of nanowire surface states (Cavallini et al., 2006) and the associated persistent photocurrent in GaN- (Polenta et al., 2008) and ZnO-based (Hullavarad et al., 2009) nanowires.

By performing spectrally resolved scanning photocurrent microscopy, characteristics of Schottky contacts can be investigated. Schottky barriers can be extracted by following the Fowler model (Fowler, 1931) using light below the bandgap of the semiconductor. This prevents band-to-band excitations whereas excitations of charge carriers from the metal contact over the Schottky barrier can still occur (Sze & Ng, 2007). Yoon et al. showed that the Schottky barrier heights for phosphorous-doped Si nanowires are reduced compared to bulk Si (Yoon et al., 2013). The advantage of the photocurrent method compared to current–voltage or capacity–voltage measurements is that no electric bias is applied, which may change the population of interface states (Yoon et al., 2013).

The timescales of the underlying optoelectronic dynamics at nanowire surfaces and interfaces are too fast to be resolved by conventional photocurrent spectroscopy. To this end, time-resolved photocurrent spectroscopy can be applied (see Section

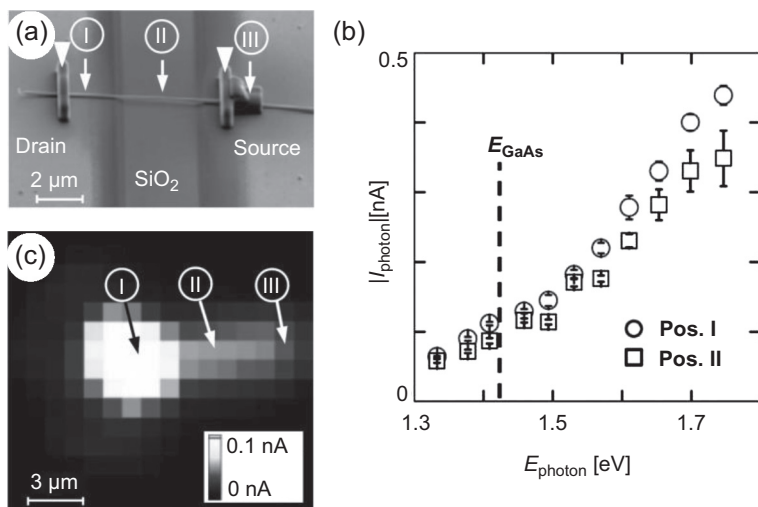


Figure 13.7 (a) SEM image of a p-doped GaAs nanowire bridging two gold electrodes. (b) Corresponding spatially resolved photocurrent map ($V = +1$ V, $T = 296$ K, $\lambda = 780$ nm, $I_{\text{Laser}} = 60$ W/cm²). (c) Photocurrent I_{photon} as a function of excitation energy E_{photon} for position I (circles) and II (squares) in (a). Dashed line indicates the band gap of the GaAs nanowire ($V = -1$ V, $T = 296$ K, $I_{\text{Laser}} = 100$ W/cm²).

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13.2.2), as was performed for p-doped GaAs nanowires ([Prechtel, Padilla, et al., 2012](#)) and for nominally undoped InAs nanowires ([Erhard et al., 2013](#)). Figure 13.8 shows the time-resolved photocurrent measurements on a single InAs nanowire performed with the measurement setup depicted in Figure 13.3. Each trace depicts the sampled, time-resolved photocurrent for scanning the pump laser along the nanowire from one metal contact (position 1) to the opposite contact (position 11) in 11 steps. At the nanowire–metal interfaces, a thermoelectric current is observed (triangle) which decays in the first 10 ps after pulsed laser excitation (positions 1 and 11). The dominant photocurrent contribution for long timescales is the drift of photogenerated holes (arrow in Figure 13.8). This drift current peak shifts in time for scanning the pump laser along the nanowire from one contact (position 1) to the second contact (position 11) (cf. Figures 13.3 and 13.8(a)). From this time-of-flight analysis, one can deduce a hot hole drift velocity of about 3×10^6 cm/s, which is consistent with the group velocity of the photogenerated holes ([Erhard et al., 2013](#)). The current of the photogenerated electrons can be detected in the first picoseconds where a THz oscillation due to a photo-Dember effect occurs (circle in Figure 13.8), which can be explained by the larger diffusivity of the photogenerated electrons compared to one of the holes ([Dember, 1931](#)).

GaAs nanowires can also exhibit a photo-thermoelectric current if the nanowire–metal interfaces are nearly ohmic ([Prechtel, Padilla, et al., 2012](#)). In the case of a Schottky contact, an ultrafast displacement current can occur with a full width of half maximum of 1.5 ps ([Prechtel, Padilla, et al., 2012](#)).

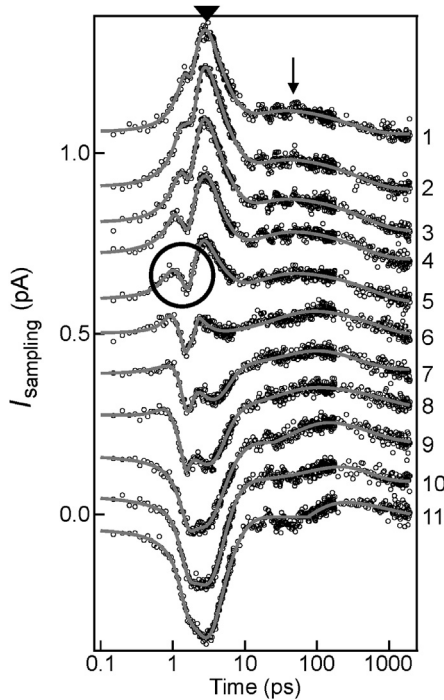


Figure 13.8 Time-resolved photocurrent I_{Sampling} for different pump laser positions along a single InAs-nanowire scanning the pump laser from one contact to the other (cf. inset Figure 13.3). Lines are fits to the data (Erhard et al., 2013). All data have an artificial offset for clarity. ($\lambda = 780$ nm, $P_{\text{Pump}} = 6.4$ kW/cm², $P_{\text{Probe}} = 3.2$ MW/cm², $T_{\text{Bath}} = 77$ K). Erhard et al. (2013) © 2012 by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

13.5.3 Radial geometries

Recently, GaAs/AlGaAs core-shell nanowires have been increasingly investigated by photocurrent measurements as the AlGaAs shell reduces the Fermi-level pinning at the nanowire surface (Chang et al., 2012; Demichel et al., 2010; Parkinson et al., 2009; Rudolph et al., 2013). Additionally, the AlGaAs shell influences the polarization dependence since the material changes the dielectric confinement. The polarization anisotropy ρ (cf. Section 13.4) is larger for photon energies where only the GaAs core is excited compared to the case where the nanowire core and shell are excited (Persano et al., 2011). Kim et al. studied ρ for excitation close to the GaAs core bandgap. They found four different regions for ρ in wurtzite GaAs/AlGaAs core-shell nanowires (Figure 13.9) (1) For excitation below the bandgap of GaAs, photocurrents are dominated by defect states (Urbach tail) and the polarization anisotropy is positive due to dielectric mismatch (Section 13.4). (2) Near the bandgap, the Franz Keldysh effect becomes more pronounced and the polarization anisotropy is negative as it is dominated by the optical selection rules of the involved bands. (3) For higher photon energies, band-to-band transitions dominate the photocurrent and the dielectric

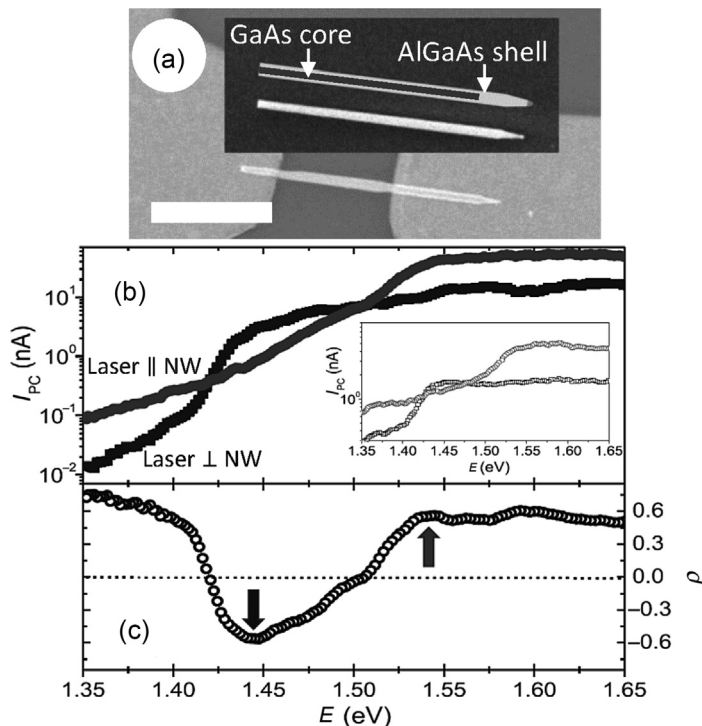


Figure 13.9 (a) SEM image of a GaAs/AlGaAs core-shell nanowire before (top) and after the fabrication of gold contacts. Scale bar 1 μm (b) and (c) Photocurrent I_{PC} and polarization anisotropy ρ as a function of excitation energy E . Inset: Photocurrent I_{PC} for a single wurtzite GaAs nanowire without shell. ($V = 5\text{ V}$, room temperature, $P = 45\text{ }\mu\text{W}$).

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mismatch leads to a positive polarization anisotropy (Kim et al., 2013). For low temperatures, the optical selection rules of the Franz Keldysh effect were used to determine the valence band splitting between heavy hole and light hole to be in the range of 90 meV (Kim et al., 2013). Combining photocurrent spectroscopy and photoluminescence measurements on GaAs/AlGaAs core-shell nanowires, Chen et al. derived the band edge discontinuity in the conduction band ΔE_C between the GaAs core and the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ shell for different x , varying from about 0.17 meV for $x = 0.24$ to about 0.28 meV for a pure AlAs shell (Chen et al., 2013).

13.5.4 Axial geometries

Axial heterojunction nanowires have the advantage that they can serve as a building block for multijunction solar cells (Yao et al., 2014). Recently, Yao et al. reported an efficiency of 7.58% for GaAs nanowire array solar cells by optimizing the array structure. A pin junction close to the nanowire tip was observed to be favorable, as the carrier generation hot spot is located close to the nanowire tip due to the high

absorption coefficient of GaAs. For higher photon energies, the surface recombination of the photogenerated charge carriers is enhanced, resulting in a smaller external quantum efficiency for short wavelengths (Yao et al., 2014).

Moreover, zero-dimensional quantum-confined structures have been realized in axial geometries affecting the optical and the transport properties of a nanowire. Both can be investigated by photocurrent spectroscopy. This has been done for avalanche photodiodes consisting of an InP nanowire with a single quantum dot in the axial pn junction (Figure 13.10). The photocurrent spectra in Figure 13.10(c) give evidence of the s, p, and d-shell of the quantum dot, making it possible to electrically detect a single exciton in a nanowire-based quantum dot (Bulgarini et al., 2012).

Rigutti et al. showed that the photocurrent to dark current ratio can be enhanced by introducing AlN quantum disks into a GaN nanowire. On the one hand, the introduced axial quantum disc heterostructure acts as a barrier for the dark current. On the other

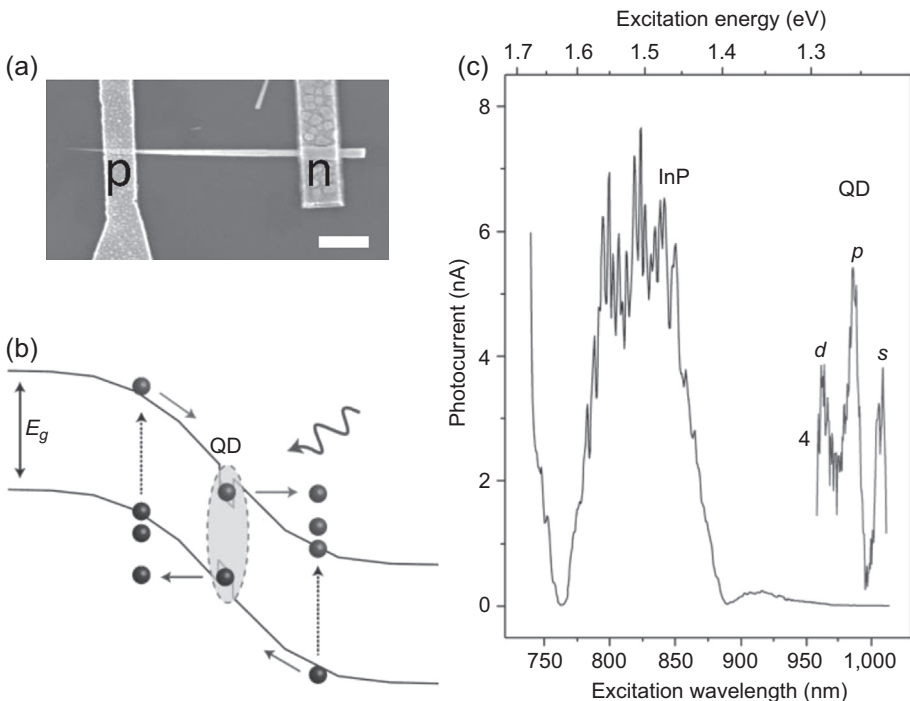


Figure 13.10 (a) SEM image of the investigated InP nanowire device. Scale bar 1 μm . (b) Schematics of carrier multiplication starting from an exciton generated in a nanowire QD, followed by tunneling in the nanowire avalanche region. (c) Photocurrent spectroscopy at $V_{\text{sd}} = -2$ V with 1 μW (InP data) and 20 μW (QD data) excitation powers. Band-edge absorption in the nanowire is observed around 825 nm. Absorption in the QD s-, p-, and d-shells is observed at longer wavelengths.

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hand, piezoelectric fields support the extraction of photogenerated charge carriers from the quantum discs due to quantum-confined stark effect (Rigutti et al., 2010).

13.5.5 Nanowire hybrid structures

For some applications, it can be beneficial to use a hybrid structure consisting of semiconductor nanowires and a second material. Over the last years, many hybrid structures have been introduced and investigated with regard to photovoltaic devices. The large interface in the nanowire hybrid structures is exploited for efficient separation of photogenerated electrons and holes. At the same time, the nanowires act as good transport channels for photogenerated charge carriers to the electrodes (Leschkies et al., 2007; Ren et al., 2011; Shiu, Chao, Hung, Yeh, & Lin, 2010; Unalan et al., 2008). Leschkies et al. showed that the combination of ZnO nanowires with CdSe (Leschkies et al., 2007) or PdSe (Leschkies, Jacobs, Norris, & Aydil, 2009) quantum dots (nanoparticles) extends the device absorption and enhances the photon-to-current conversion efficiency. Hereby, the photogenerated electrons in the quantum dot are efficiently extracted and transported to the electrodes by the ZnO nanowires (Leschkies et al., 2007). A similar behavior was observed for nanowires combined with organic materials such as polymers (Ren et al., 2011; Shiu et al., 2010). Exploiting the fact that ZnO nanowires can be grown on single-walled carbon nanotube films, semiconductor nanowires are candidates for flexible photovoltaic devices (Unalan et al., 2008). Functionalizing nanowire surfaces with molecules may lead to new sensor applications. For example, a Si nanowire field-effect transistor coated with porphyrin molecules enables the photoinduced electron transfer from the porphyrin to the nanowire, as in artificial eyes (Winkelmann et al., 2007). In addition, a nanowire can act as a near-field detector of optical plasmons. By performing polarization-dependent photocurrent measurements, this was shown for an Ag nanowire crossing an electrically contacted Ge nanowire. Here, one uses the fact that a surface plasmon polariton in an Ag nanowire can generate electron hole pairs in a Ge nanowire (Falk et al., 2009).

13.6 Conclusion and future trends

Semiconductor nanowires have unique absorption and photocurrent characteristics due to their geometry. Therefore, nanowires are good candidates for many future applications. The enhanced absorption in nanowires, the ability to build radial or axial pn junctions, and the possibility to combine them with organic and nanoparticle solar cells may help to build cost-effective photovoltaic devices above the Shockley-Queisser limit. The capability to generate (Erhard et al., 2013; Seletskiy et al., 2011) and detect (Vitiello et al., 2012) THz radiation in nanowires makes them interesting for THz applications. Furthermore, nanowires are a possible building block for integrated photonic circuits, as one can build LEDs or photodiodes based on a single nanowire (Tchernycheva et al., 2014). Nanowires exhibit a fast photoresponse down to the picosecond regime, and they allow detecting single exciton states in quantum dots,

which can be exploited in future quantum technologies (Bulgarini et al., 2012). The small size and the principally small power consumption of nanowires make it feasible to build devices that can be embedded in everyday life objects such as wristwatches or cell phones (Yang, Yan, & Fardy, 2010). To make this all come true, further improvement of the nanowire material and the nanowire device performance has to be achieved. Photocurrent measurements help to characterize and understand the nanowire devices and to identify future device geometries and applications.

13.7 Sources for further information

A summary regarding the optimization of nanowire photovoltaic devices can be found in Garnett et al. (2011). Measurements with respect to photovoltaic performance on a single nanowire device are reviewed in Tian, Kempa, and Lieber (2008). Further information about nanowire solar cells and thermoelectric devices can be found in Hochbaum and Yang (2010). Nanowire properties and devices with respect to photodetection applications are discussed in Soci et al. (2010) and VJ et al. (2011). Nanowire photodetectors and photovoltaic devices are reviewed together with other photonic nanowire devices in Li, Qian, Xiang, and Lieber (2006) and Yan, Gargas, and Yang (2009). Further information about ultrafast carrier dynamics in semiconductor nanostructures can be found in Shah (1996).

Acknowledgements

We thank L. Pecht, S. Thunich, S. Hertenberger, P. Seifert, D. Spirkoska, H. Karl, C. Ruppert, M. Betz, G. Abstreiter, A. Fontcuberta i Morral, J. J. Finley, and G. Koblmüller for very fruitful collaborations and the ERC Grant NanoREAL (n°306754) for financial support.

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Cathodoluminescence microanalysis of ZnO nanowires

14

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14.1 Review of the cathodoluminescence technique

Luminescence spectroscopy has been developed into standard analytical techniques in various fields of materials science and technology. Of these, scanning cathodoluminescence (CL) microscopy has emerged as a powerful method to non-destructively image and analyse, in 3D, dopants, point and extended structural defects as well as impurities at nano-scale spatial resolution with very high detection sensitivity (Yacobi & Holt, 1990). A CL system normally entails a scanning electron microscope (SEM) equipped with a parabolic light collector positioned above the sample, optical monochromators and a hot/cold sample stage (see Figure 14.1). The SEM is used to raster over the surface of the sample a highly focussed electron probe with a sub-3-nm diameter, d_p , and a variable energy, E_o , of 1–30 kV. The observed CL spatial resolution and analysis depth in bulk samples is determined by E_o , d_p , the stopping power of the sample (its composition) and the recombination length, L , of carriers in the sample, which is determined by their lifetime, τ , and mobility, μ , with $L = \sqrt{\frac{k_B T}{e}} \mu(T) \tau$. At low voltages (<1 kV), the size of the beam interaction volume at the sample surface is less than 10 nm and can be considered as a point source of injected carriers. For highly luminescent samples the CL spatial resolution is determined by L only and sub-50-nm CL spatial resolution can be achieved in wide bandgap semiconductors,

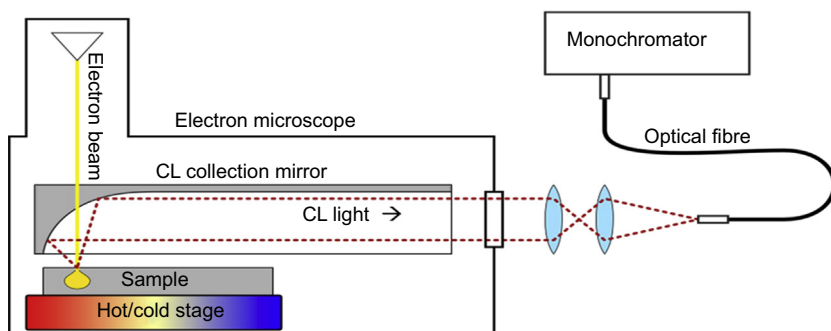


Figure 14.1 Schematic representation of a typical CL system with the parabolic mirror for collection. The optical fibre guides the collected light either to a monochromator or directly to a photodetector.

such as ZnO and III-nitrides (Fleischer et al., 1999), which are typically characterised by short carrier recombination lengths (<100 nm). In weakly luminescent specimens, the electron beam current must be increased to maintain a sufficient CL signal-to-noise ratio, which leads to a greater d_p and a lower CL spatial resolution. For semiconductors with a high refractive index, large-beam currents are often necessary, as nearly all of the generated CL is internally reflected into the sample and only a small fraction (3.8% for planar ZnO with $n = 2.4$) of the light exits the surface for collection in an escape cone whose central angle is determined by the refractive index, n , of the sample (Yacobi & Holt, 1990). It is also important to note that the parabolic CL collection mirror efficiently collects all generated light over a circular area of ~ 100 nm in diameter, regardless of the beam interaction volume. This means that scattered or reflected light modified by internal absorption or light remotely fluoresced in the sample can also contribute to the total measured CL at the electron beam irradiation point.

When a focussed electron beam irradiates a sample, all of its energy is dissipated by inelastic electron scattering events that, in most cases, ultimately result in single electron transitions, promoting electrons from the valence band (VB) to the conduction band (CB). Figure 14.2 shows the possible recombination channels as a result of an electron–hole (e–h) pair excited by an electron beam. The excited e–h pairs consequently thermalise to the band edges, where they recombine via a number of different recombination channels producing either phonons (non-radiative) at structural dislocations or CL (radiative) at neutral donors and acceptors. The latter process can occur either at single centres as free-to-bound transitions or at a neutral donor–neutral acceptor pair in close proximity to each other as a donor–acceptor pair (DAP) transition. Additionally, signature CL can be produced via e–h recombination at point defects, transition metals and rare earth elements through the excitation and radiative decay of 1s, 3d and 4f electrons in each of these centres, respectively. E–h pairs can become correlated through the Coulombic attraction-forming charge-neutral quasi-particles known as excitons. This occurs when the electrostatic binding energy, E_B , of the e–h pair is sufficiently large compared with the thermal energy ($k_B T$) of the

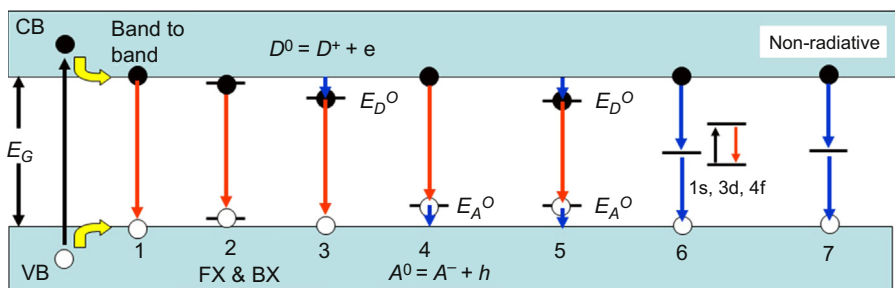


Figure 14.2 Schematic diagram of the recombination channels possible as a result of an excitation of an electron–hole pair. 1. Band-to-band transition. 2. Recombination of free and bound excitons (FX and BX). 3. Neutral donor to free hole. 4. Free electron to neutral acceptor. 5. Donor–acceptor pair transition. 6. Internal transitions within emission centres in point defects, transition metals or rare earth elements. 7. Non-radiative recombination.

sample. These free excitons thermalise via phonon scattering to the Γ point, where they radiatively recombine with high efficiency, emitting CL at an energy of $E_G - E_B$, where E_G is the bandgap energy. Excitonic CL emission can be observed at room temperature and above in wide-bandgap materials, which normally have large exciton-binding energies, e.g. ZnO with $E_B = 60$ meV (Thomas, 1960). At low temperatures, 10–80 K, excitons can become localised at neutral donors and acceptors and at extended structural dislocations. These bound exciton transitions produce very sharp characteristic CL emission, as they do not involve phonons and can be used to identify and characterise specific near band edge (NBE) centres and map their 3D distribution and relative concentrations. Temperature-resolved CL and power density-resolved CL, where the beam current is systematically varied, can be both used to characterise and assign CL emission peaks to specific defect centres and dislocations.

CL spectral maps where a complete CL spectrum is taken at each image pixel can be used to establish correlation and anti-correlation between CL peaks in a particular sample. These data can be spatially correlated with other available SEM analytical signals to assist with establishing the origin of the CL emission; these include characteristic X-rays, electron backscatter diffraction and back scattered electrons. Furthermore, collection of these large CL data cubes, measured as function of both temperature and power density, has opened the door for statistical analysis that often reveals subtle variation in defects distributions that is not observed with conventional monochromatic (single wavelength) or panchromatic (all wavelengths) CL imaging.

Recent CL imaging and spectroscopy studies of ZnO nanowires will be presented to illustrate and explain the standard CL techniques and analytical methods. This particular can be considered to be an exemplar of how CL microscopy and microanalysis can be used to investigate and characterise nanowires of all types of materials. High CL spatial resolution can also be achieved in isolated nanostructures at all electron beam voltages in transmission mode as the beam passes through these electron transparent samples with virtually no beam spreading. This CL technique is conducted in either a SEM or in a transmission electron microscope (TEM) operating in scanning (STEM) mode, with the sample supported on a holey carbon film to eliminate spurious CL generated from backscattered electrons from the substrate.

14.2 Brief overview of luminescence centres in ZnO

ZnO is a II–VI direct, wide-bandgap semiconductor ($E_G = 3.35$ eV at 300 K, high refractive index ~ 2.0), which exhibits interesting optoelectronic properties. The large exciton-binding energy (60 meV) of ZnO leads to efficient optical emission at room temperature, making it an attractive candidate for light-emitting devices and applications that require strong visible luminescence. Both ZnO bulk and nanostructures can possess a large number of native defects and extrinsic impurities that are optically active, emitting light over a wide spectral range from ultraviolet to red (Djurisic et al., 2007; Willander et al., 2009). As ZnO is a naturally n-type, the realisation of p-type doping has proved to be extremely difficult. Several research groups have reported the fabrication of p-type ZnO, but the results are difficult to reproduce

and remain a matter of great controversy. In addition, ZnO offers advantages of having a rich family of nanostructures such as nanowires, nanorods, nanobelts and nanosprings (Wang, 2004). These nanostructures possess a large surface area-to-volume ratio, enabling them to release stress and strain when growing on a lattice-mismatched substrate (Perillat-Merceroz et al., 2012). A variety of ZnO nanowire and nanorod structures have been reportedly created by high-temperature vapour-phase transport (Huang, Mao, et al., 2001; Huang, Wu, et al., 2001), via a vapour–liquid–solid (VLS) or vapour–solid (VS) mechanism (Kim, Scholz, Gosele, & Zacharias, 2008). The average diameter of ZnO nanowires typically ranges over an order of magnitude from a few nm to 200 nm; the length could be up 10 μ m, yielding an aspect ratio of 500. Room-temperature lasing action via optical pumping has been demonstrated in vertically aligned ZnO nanowire arrays grown by the catalyst-driven vapour transport method (Huang, Mao, et al., 2001).

A typical CL spectrum of ZnO is generally characterised by an NBE emission in the ultraviolet and a broad band emission due to deep-level defects. Deep-level emission (DLE) can extend from about 400 to 750 nm (3.1–1.7 eV), covering almost the entire visible range. This broad band is often a superposition of the emissions from a number of radiative recombination pathways. Various reports have suggested different defects as the origin of various visible emissions (see Table 14.1). The common DLE bands observed in ZnO are green, yellow and red luminescence. The green luminescence, which peaks between 2.3 and 2.5 eV, has been the focus of many studies but is still a subject of considerable debate. The chemical origin of this ubiquitous emission has been attributed to several native defects including oxygen vacancies (V_O) (Vanheusden, Seager, Warren, Tallant, & Voigt, 1996) and zinc vacancies (V_{Zn}) (Kohan, Ceder, & Morgan, 2000), interstitials (Zn_i , O_i) (Liu, Kitai, & Mascher, 1992) and antisites

Table 14.1 Reported emissions from ZnO and generally accepted models of defect-related transitions producing the emission bands. The conduction and valence bands are denoted as CB and VB, respectively

Emission colour	Defect-related transitions	References
Violet	Zn_i to VB	Ahn et al. (2009)
Green	V_O to VB, V_{Zn} to CB	Vanheusden et al. (1996), Kohan et al. (2000), and Ton-That et al. (2012)
Yellow	CB to Li_{Zn} or Na_{Zn} , CB to O_i	Meyer et al. (2006), Hoffmann et al. (2010), Zwingel and Gartner (1974), and Ozgur et al. (2005)
Orange/red	CB to N_O , CB to V_{Zn} , CB to O_i	Djurisic et al. (2007), Tarun et al. (2011), Alvi et al. (2011), Liu et al. (2004), and Wang et al. (2009)

(Zn_O, O_{Zn}) (Reynolds, Look, Jogai, & Morkoc, 1997). Comprehensive theoretical studies (Janotti & Van de Walle, 2007, 2009), however, revealed that the interstitial and antisite defects are unlikely the cause of green luminescence since they have either too high formation energies (O_i, Zn_O and O_{Zn}) to occur in significant concentrations, or form a shallow level (Zn_i). There could be multiple emissions in the green spectral range (Borseth et al., 2006). More recently, the green emission has been explained as arising from more than one deep-level defect (Ton-That, Weston, & Phillips, 2012). In this investigation, V_O and V_{Zn}, a deep donor and acceptor respectively, were found to produce green CL at slightly different wavelengths (Ton-That et al., 2012). This phenomenon is the main cause of discrepancy in assigning DLE in ZnO to specific defects. The yellow luminescence in ZnO at 2.1–2.2 eV was first observed in Li-doped (Hoffmann, Malguth, & Meyer, 2010; Meyer, Hofstaetter, & Laguta, 2006) and Na-doped ZnO (Zwingel & Gartner, 1974). These studies established the similarity between Li_{Zn} and Na_{Zn}, which both act as deep acceptors located at about 0.8 eV above the VB and are often involved in DAP recombinations with a variety of shallow donors. These centres exhibit strong exciton–phonon coupling, with the Huang-Rhys factor being in the range of 13–17 (Hoffmann et al., 2010). Yellow emission has also been attributed to O_i (Ozgur et al., 2005). It was reported that ZnO exhibits yellow emission upon irradiation with a He–Cd laser, and that this emission is saturated at a low excitation density ($\sim 10^{-3}$ W/cm²), suggesting that O_i is formed at a low concentration. The orange emission, which is rarely observed in ZnO, has been proposed to be related to V_{Zn} (Djurisic et al., 2007), while the red emission has recently been assigned to nitrogen defects (Tarun, Iqbal, & McCluskey, 2011), O_i (Alvi, ul Hasan, Nur, & Willander, 2011; Liu, Wu, Cao, & Chang, 2004) and V_{Zn} defect centres (Wang, Vlasenko, Pearton, Chen, & Buyanova, 2009). It has been reported that violet DLE at 3.1 eV in ZnO thin films was due to Zn_i (Ahn, Kim, Kim, Mohanta, & Cho, 2009); this assignment is compatible with the predicted ionisation energy (30 meV) for this donor defect (Look, Hemsky, & Sizelove, 1999).

14.2.1 Spatially resolved cathodoluminescence analysis of defects

The depth distribution of luminescence centres or defects in a specimen can be determined by measuring CL spectra as a function of the excitation depth. The most convenient way of carrying out depth-resolved CL analysis is to use the constant power method (Fitting et al., 2002), in which the acceleration voltage, V_B , is varied systematically, while the beam current, I_B , is adjusted so that the beam power ($V_B \cdot I_B$) is kept constant. In this way, CL data can be acquired systematically from different depths within a specimen while the electron–hole pair generation rate is kept unchanged. Depth information of luminescence signals can be obtained and the average depth of luminescence centres can be determined by comparing depth-resolved spectra with simulated electron loss profiles using Monte Carlo techniques (Drouin et al., 2007). Figure 14.3 shows the lateral and depth profiles calculated for ZnO for an acceleration voltage of 5 kV, together with the trajectories of 5000 incident electrons in ZnO at 5 kV modelled through the Monte-Carlo simulation CASINO

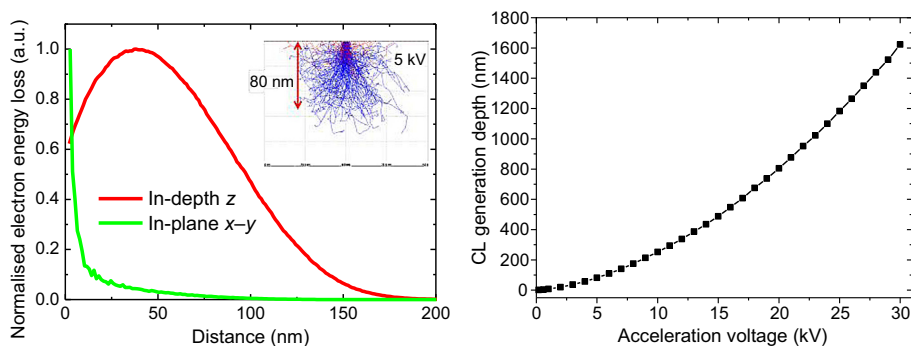


Figure 14.3 (Left) Lateral and depth profiles of the electron energy loss in ZnO modelled through the Monte-Carlo simulation CASINO. The CL generation depth, taken as the thickness of the surface layer in which 70% of the CL intensity is generated, is 80 nm at $V_B = 5$ kV. Inset shows the trajectories of incident electrons in ZnO. (Right) Stimulated dependence of the CL generation depth on the acceleration voltage for ZnO.

(Drouin et al., 2007). In depth-resolved CL measurements, the acceleration voltage is typically varied between 1 and 30 kV, which corresponds to the respective average generation depths of 8 nm and $1.6\ \mu\text{m}$ in ZnO (Figure 14.3). The precision of CL generation excitation depth is also dependent on the diffusion of secondary electrons, which was taken into account in the CASINO simulation. To investigate the depth-dependent luminescence properties of individual nanowires, one needs to ensure that the CL excitation volume does not exceed the size of a nanowire. Otherwise forward-scattered primary electrons will excite CL in surrounding nanowires, which will then contribute to the total CL signal measured at the analysis point. This effect can be very significant in ZnO nanowires where their axial surface is decorated with highly luminescent deep-level defects.

In this work, ZnO nanowires were grown by the VS method using a ZnO/C powder mixture heated at 950°C as source material. The sapphire ($11\bar{2}0$) substrate, which had been pre-deposited with a 3-nm thin layer of gold, was placed downstream in a gas-controlled horizontal furnace at a lower temperature. Using this growth technique, the nanowire morphology and defect chemistry could be controlled by varying the growth temperature ($700\text{--}900^\circ\text{C}$) in combination with the flow rate of oxygen carrier gas. The grown nanowires were found to be vertically aligned with the c -axes of the nanowires perpendicular to the substrate surface, as shown in Figure 14.4. The SEM image reveals the hexagonal symmetry of the nanowires and that most of the ZnO nanorods grew perpendicular to the substrate. Conventional ($\theta\text{--}2\theta$) XRD on the sample verifies the SEM result, showing that the vertically aligned nanowires are oriented in the $[0001]$ ZnO direction parallel to the $[11\bar{2}0]$ sapphire substrate.

Figure 14.5 presents the room temperature CL spectra obtained from individual nanowires dispersed on a substrate. To facilitate CL depth-resolved measurements, nanowires were removed from the growth substrate by sonication and dispersed onto a new Si substrate. CL exhibits similar luminescence signals among ZnO nanowires with strong green luminescence emission at ~ 2.4 eV; however, the relative

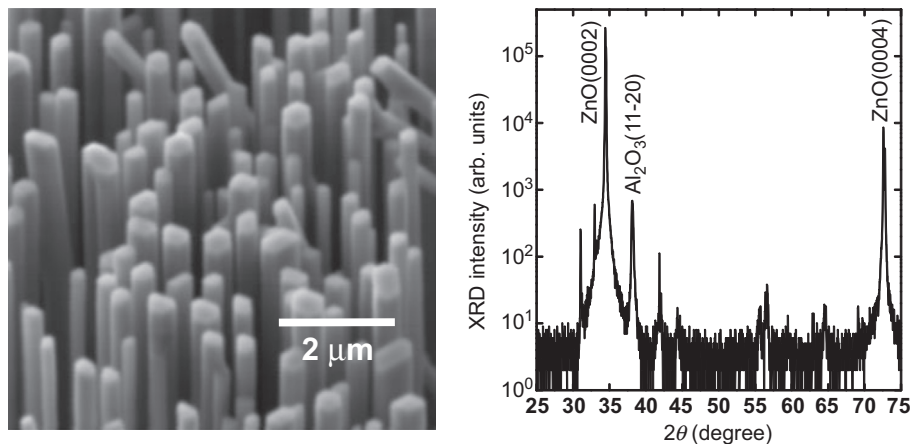


Figure 14.4 (Left) SEM image of ZnO nanowires grown by the Zn vapour transport method on a sapphire substrate. (Right) Typical X-ray diffraction profile showing the nanowires have a *c*-axis orientation.

intensities of the emission bands vary considerably with acceleration voltage. The CL generation depth increases with the acceleration voltage, with depths of 82 and 252 nm for acceleration voltages of 5 and 10 kV, respectively. At 5 kV, the green emission is the more efficient recombination channel, indicating the shell of the nanowire is rich in deep-level defects. Increasing the acceleration voltage to 10 kV enhances both NBE and green emissions as expected; however, the nanowire now exhibits a robust NBE emission. The relatively strong NBE at 10 kV indicates that the nanowire possesses higher crystal quality in the core, as shown in the simulation. This result is consistent with previous findings that the green luminescence in ZnO nanostructures originates from the surface (Prades, Cirera, Morante, & Comet, 2007; Ton-That, Phillips, Foley, Moody, & Stampfl, 2008).

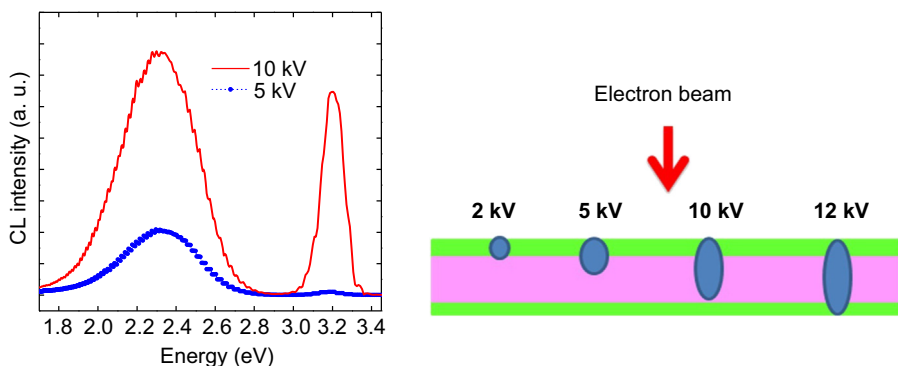


Figure 14.5 (Left) Room-temperature CL spectra obtained at acceleration voltages of 5 and 10 kV from a ZnO nanowire of 300 nm diameter. (Right) Schematic illustration of CL generation profiles in the nanowire at various acceleration voltages simulated using CASINO.

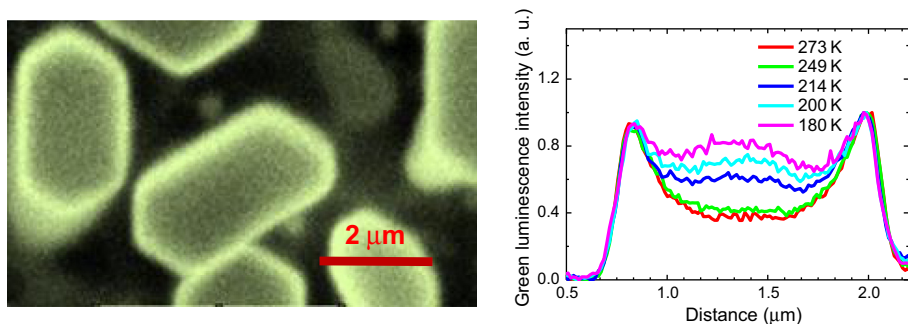


Figure 14.6 (Left) Top-view monochromatic CL image of ZnO nanowires acquired at 8 kV. (Right) Normalised line profiles of green intensity obtained from the CL image, showing the enhancement of green luminescence from the nanowire shell.

The inhomogeneous distribution of the green luminescence centres in ZnO nanowires is illustrated more clearly in Figure 14.6, which shows a monochromatic CL image recorded at a photon energy of 2.42 eV together with the line profiles of green intensity across a nanowire diameter at various temperatures. The nanowire shell of a thickness about 100 nm exhibits remarkably stronger green luminescence. The green emission in the core of the nanowire decreases with increasing temperature from 180 to 273 K, presumably due to less efficient green recombination centres at higher temperatures (see the following section). The other possibility is the re-absorption of NBE emission, which leads to the excitation of surface green centres at the tip of the nanowire. The monochromatic CL images demonstrate that low-level luminescence signals from nanostructures can be obtained and that CL can provide a direct comparison of local optical properties of ZnO nanowires by minimising any possible external perturbations, such as effects of a non-uniform excitation density throughout the electron–solid interaction volume. All nanorods can be clearly resolved as individual emitters and this represents a significant advance over the conventional photoluminescence (PL) method, which provides an average of a larger number of nanowires due to its poorer spatial resolution. The observed luminescence inhomogeneity could not have been distinguished without the high spatial resolution afforded by CL. Furthermore, the variation of the luminescence emission with depth and local excitation position demonstrates that a luminescence spectrum typically obtained with conventional PL may not reveal all local properties of a nanowire. Due to strong optical absorption of the ultraviolet excitation source, the PL signal is generated within the top tens of nanometers of specimens, while dimensions of the PL spot are diffraction limited, leading to PL lateral resolution of >200 nm.

14.2.2 Dependence of excitation density

To understand the emission properties of ZnO nanowires, it is necessary to assess the effect of e-beam excitation conditions on CL data. In power density-resolved CL measurements, the acceleration voltage, and hence the CL generation depth, is kept

constant while the beam current is varied. The number of e–h pairs generated is proportional to the beam power and hence the beam current. The power-law dependence of the CL intensity on beam current ($I_{CL} \propto I_B^n$, where I_{CL} is the integrated intensity of an emission band), as a measure for CL kinetics (Phillips, Telg, Kucheyev, Gelhausen, & Toth, 2003; Lem, Phillips, & Ton-That, 2014), can be determined, providing an insight into the nature of a recombination process.

With the Bohr radius of only 2.3 nm (Gu, Kuskovsky, Yin, O'Brien, & Neumark, 2004), ZnO nanowires with diameters of tens of nanometres will not display quantum size effects. The CL properties of an ensemble of large ZnO nanowires are generally similar to those of bulk ZnO. It is known that the characteristics and chemical nature of green luminescence centres vary widely, depending on ZnO growth method and processing conditions (van Dijken, Meulen Kamp, Vanmaekelbergh, & Meijerink, 2000). CL spectra are generally required to be deconvoluted in order to extract the intensities of individual bands within the broad DLE. To resolve overlapped green and yellow emissions in hydrothermal ZnO, curve-fitting analysis was applied using nonlinear regression. Two methods were employed to determine the peak parameters of the emission bands. These methods are illustrated in Figure 14.7, which shows the CL spectra of the as-grown and Li-doped ZnO, acquired with different beam currents (acceleration voltage is fixed at 15 kV). The first method involved doping ZnO by the in-diffusion of Li at 700 °C to increase the Li concentration until the yellow emission completely dominates the DLE. In the second method, CL spectra were acquired with the lowest possible beam current (in the pA range), at which the yellow emission

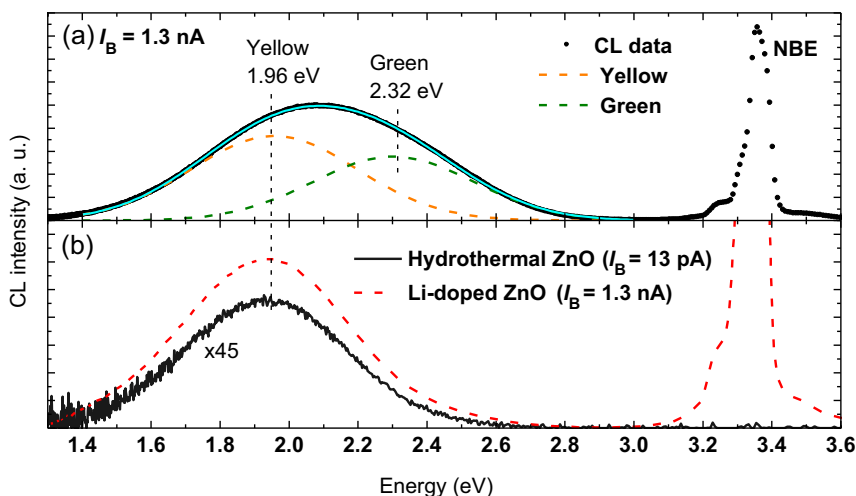


Figure 14.7 (a) Deep-level visible spectrum of hydrothermal ZnO ($E_B = 15$ keV) with fitted green and yellow bands centred at 2.32 eV and 1.96 eV, respectively. The peak parameters of the yellow band were obtained from the CL spectrum of the Li-in diffused ZnO, which exhibits only yellow luminescence, as shown in (b). Yellow-only CL emission could also be generated in hydrothermal ZnO when low beam currents ($I_B < 50$ pA) were used.

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due to Li impurities is the most efficient recombination channel due to abundant Li in hydrothermal ZnO. Both methods yield an identical profile for the yellow emission (Figure 14.7(b)), with peak energy of 1.96 eV and FWHM of 0.58 eV at 80 K. This yellow band is similar in energy position and peak shape to the PL spectrum of Li-containing ZnO (Hoffmann et al., 2010; Rauch et al., 2010), confirming the chemical origin of the yellow emission. By constraining the yellow parameters, this approach provides unique fitting solutions for all DLE spectra of ZnO. The parameters of the green band at 80 K are peak energy 2.32 eV and FWHM 0.51 eV. These peak parameters are comparable to those reported previously for the V_{Zn} -related GL in ZnO (Hoffmann et al., 2010; Ton-That et al., 2012). The wide FWHM of the intrinsic defect-related GL band is likely due to the presence of multiple radiative centres that involve V_{Zn} complexes, which have slightly different energies within the bandgap (Dong, Tuomisto, Svensson, Kuznetsov, & Brillson, 2010).

The intensities of the NBE, green and yellow emissions of hydrothermal ZnO were found to increase at different rates as the beam current I_B was increased in the range 0.01–10 nA. This excitation density-dependent behaviour is presented in the log–log plots in Figure 14.8, which shows the integrated intensity of each emission versus I_B at 10, 80 and 300 K. Varying I_B in this range did not introduce any noticeable changes in peak energy or shape, except for the relative intensities of the emission bands, indicating that the exciton–exciton scattering loss is insignificant under the typical CL excitation conditions (Ozgur et al., 2004). With increasing I_B , the green emission increases at a faster rate than the yellow. The excitation dependence was analysed for all of the data set using the power law model, yielding the values of the exponent shown in Table 14.2.

The variations of the CL intensities of the NBE, green and yellow bands with beam current exhibit three noteworthy features:

1. The NBE emission of ZnO exhibits linear or slightly superlinear dependence on power excitation density under typical CL excitation conditions at any temperature between 10 and 300 K.
2. Both green and yellow emissions exhibit a close to square root dependence on power density at 300 K, while the green exhibits a linear relationship with the excitation density at 10 K.
3. The DLE of hydrothermal ZnO is dominated by the Li yellow emission at 10 and 80 K, especially when small I_B (pA level) is used. On the other hand, the DLE is predominantly green at 300 K.

The linear relationship between the NBE emission and I_B is characteristic of excitonic recombinations (Phillips, 2006). The sub-linear dependency of the DLE bands on excitation density is related to a finite population of luminescence centres and their lifetimes (Phillips, 2006), and can be qualitatively explained in terms of the saturation of recombination centres with increasing I_B (Ton-That et al., 2012). Li is known to be abundant in hydrothermal ZnO with a typical concentration of $10^{18}/\text{cm}^3$ (Hoffmann et al., 2010). The Li-related DAP recombination lifetime is determined by the relaxation of holes from the VB of the Li_{Zn} acceptor state, which has a relaxation time on the order of μs (Hoffmann et al., 2010), significantly longer than the nanosecond lifetime of V_{Zn} centres in ZnO (Djurisic et al., 2007; Lettieri et al., 2009). The fast saturation

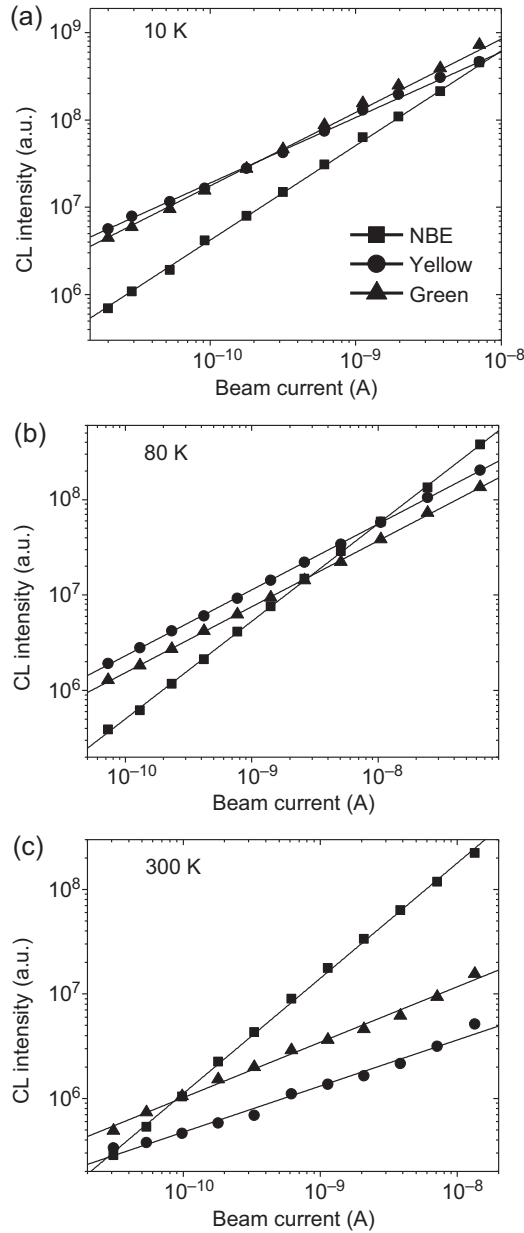


Figure 14.8 Log–log plots of the integrated intensities of the NBE, green and yellow bands as a function of electron beam current obtained from hydrothermal ZnO at (a) 10 K, (b) 80 K and (c) 300 K. Solid lines are power law fits ($I_{CL} \propto I_B^n$) to the data.

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Table 14.2 Power law exponent, n , for the $I_{CL} \propto I_B^n$ power relationship for hydrothermal ZnO at 10, 80 and 300 K

	10 K	80 K	300 K
NBE	1.10 ± 0.05	1.02 ± 0.03	1.10 ± 0.02
Yellow	0.75 ± 0.05	0.68 ± 0.03	0.51 ± 0.02
Green	0.91 ± 0.08	0.78 ± 0.05	0.57 ± 0.02

of the yellow emission with increasing I_B is due to the slow relaxation of Li_{Zn} centres, even though Li exists in a high concentration. At room temperature, the yellow luminescence scales as the square root of beam current. The green luminescence is significantly stronger than the yellow at high beam currents (>1 nA) due to two competitive recombination channels with considerable differences in recombination efficiencies. The sub-linear dependencies of the green and yellow emissions are consistent with previous PL investigations, which showed a linear dependence remained only at very low excitation levels (Guo, Qiu, & Wong, 2003). Using the bimolecular recombination equations for the band-to-band and band-to-acceptor, as detailed in Ton-That et al. (2012), the population of green centres is found to be on the order of $10^{16}/\text{cm}^3$ at 80 K, which is about two orders of magnitude lower than the Li concentration in hydrothermal ZnO. These kinetic behaviours of CL emissions demonstrate the importance of assessing the excitation conditions when CL is used to examine defect concentrations and distribution in ZnO.

From the practical point of view, it is interesting to note that the green luminescence is totally dominant over the yellow emission in hydrothermal ZnO at room temperature. However, at 80 K or lower temperatures, the yellow emission is significantly stronger, especially at low CL excitation levels ($I_B < 50$ pA), at which the Li_{Zn} emission centres are not saturated by the electron beam. This colour-tuning capability of ZnO could be utilised in visible light emitters.

14.3 STEM cathodoluminescence

Individual ZnO nanowires can be imaged and analysed in a TEM operating in STEM mode or a SEM by sonicating nanowire assemblies in alcohol and dispersing them onto a holey carbon TEM grid, as illustrated in Figure 14.9. In STEM-CL the spatial resolution is determined by L only as there is virtually no lateral electron scattering in sub-100-nm thin samples when using high-voltage excitation (~ 30 kV in SEM and ~ 80 kV in TEM). The advantage of STEM-CL in a SEM is that it facilitates high-resolution CL imaging at greater depths than the traditional low-voltage approach (see Section 14.2.1), which is always a near-surface technique. Additionally, the CL mirror can be placed underneath the sample, enabling simultaneous imaging of the

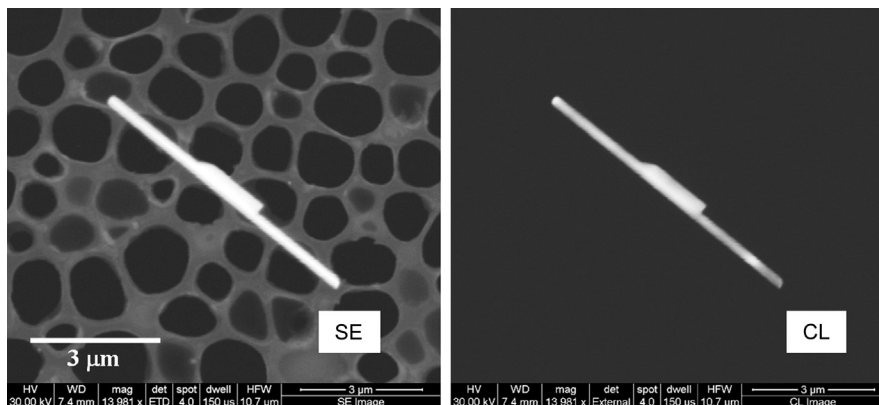


Figure 14.9 (Left) Secondary electron image of a ZnO nanowire on top of a holey carbon grid at 30 kV. (Right) Corresponding STEM-CL image showing variation in the CL intensity along the length of the ZnO nanowire and stronger CL emission at the thicker section with the remnant of a second nanowire at the centre.

other emissive SEM signals, for example secondary electrons for topography as well as backscattered electrons and X-rays for compositional information. STEM-CL in a TEM, on the other hand, provides the ability to conduct concurrent correlative CL and electron diffraction studies. This capability is particularly useful in establishing relationships between regions of non-radiative recombination and extended structural defects, such as dislocations, grain and twin boundaries and stacking faults. Lack of CL signal is the major disadvantage with STEM-CL because of the limited CL generation volume. This drawback requires the use of a high-performance parabolic mirror and efficient transmission optics to maximise the STEM-CL collection efficiency.

14.4 Conclusions

CL is a powerful microanalysis technique for the characterisation of ZnO nanowires. The main advantage of CL over the traditional PL technique is its capability of providing high spatial information on local optical and electronic properties of individual nanowires. The luminescence intensities of the defect-related green and Li-related yellow bands in ZnO nanowires are highly dependent on the excitation density and depth. Because of the considerable differences in the recombination kinetics and concentration, the intensity ratio between these bands can be manipulated by adjusting the beam current, temperature or excitation depth in nanowires during CL measurements. The feasibility of doping ZnO to very high n-type levels for plasmonic applications in the infrared spectral range has recently been demonstrated (Look & Leedy, 2013). Given the rich family of ZnO nanostructures, this material offers an exciting prospect of a new generation of plasmonic functional components that can be fabricated in a high-throughput manner.

Acknowledgements

The results in this chapter were partially contributed from our group members: Mark Lockery, Liangchen Zhu, Olivier Lee, Matthew Foley and Meng Huang, to whom we are very grateful. We would like to thank Geoff McCredie for his technical assistance.

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Part Three

Applications of semiconductor nanowires

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Semiconductor nanowires for solar cells

15

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15.1 Introduction: photovoltaic conversion for renewable energy

Solar light conversion with photovoltaic (PV) modules is an attractive means to produce clean and renewable electricity. Various technical solutions are now available on the market, with assembled silicon-based solar cells and thin films deposited on large panels. Usage is also rather versatile and systems can be adapted to different situations — from individual use with small power needs to large grid-connected PV energy plants. This allows the introduction of a wide range of technologies to the marketplace.

PV energy conversion is well established as a mandatory technology in the global energy mix that will supply our societies in the future. The PV industry has considerably changed in the last 10 years with a tremendous growing demand. Worldwide agreement such as the Kyoto Protocol (framework convention on climate change) shows the global tendency to lower fossil fuel consumption and the emission of greenhouse gases. The market has been growing regularly at a rate of about 30% over last five years for installed conversion devices, according to data from the European Photovoltaic Industrial Association (EPIA, 2014). This figure remains difficult to evaluate because the market has been very variable during this period. A deep transformation of the PV industrial scene arises from the wide deployment of PV modules — small and local industrials have been replaced with big factories usually located in Asia. This rapid evolution has come along with a drastic cut in the production cost of silicon solar cells. Production capacity has reached 40 GW per year.

Depending on its manufacturing technology, a solar panel needs a given amount of raw material and energy to get fabricated. This initial energy stake is generally reimbursed within a few years of electricity production (De Wild-Scholten, 2013). The value depends strongly on the fabrication technology and on the usage of the PV products. Concerning materials, some technologies are based on rather rare elements such as indium or tellurium. Silver is widely used for electrical contacts, and its availability is not certain for long-term periods. Total available raw materials quantities have been evaluated and global PV capacities is limited from this point of view (Jeffries, 2013; Wadia, 2009). PV cell research and development targets a compromise between lower materials consumption and higher conversion efficiency.

15.2 Solar cell devices and technologies

15.2.1 Photovoltaic conversion basics

PV devices and systems allow the direct conversion from incident light into electricity. This phenomenon occurs in an active material that usually is a semiconductor. The PV cell is exposed to light rays ideally perpendicular to the propagation direction. The amount of absorbed energy depends on the depth of the active material and on its intrinsic absorbance for the solar spectrum.

To limit material costs, we select semiconductors with highly appropriate optical and spectral characteristics and high availability on the market. Silicon is one of the most abundant elements in the earth's crust, and it presents suitable absorption characteristics regarding the sun's emission spectra. The value of its bandgap (1.1 eV) is close to the optimum value for a single absorber PV device ([Shockley & Queisser, 1961](#)). On top of that, silicon and its compounds have been widely used in microelectronics devices and for metallurgical alloys. Laboratories and industries have gathered a lot of basic knowledge and processing experience on this particular element. Despite mid-level properties from a theoretical point of view (as indirect energy bandgap that lowers the light absorption property), silicon wafers remain a preferred material for PV application. Although alternative compounds such as cadmium telluride (CdTe) or copper indium gallium selenide (CIGS) have appeared on the market, 90% of PV cell manufacturing is still made of silicon.

The first step in the PV conversion process is light absorption. Photon energy absorption leads to excitation of electrons to various energy levels in the active material. In semiconductor materials, the photon energy can be sufficient to produce a free electron that will travel in the crystalline structure. The atom that loses an electron shows a positive charge known as a hole. Electron and hole form an exciton that is rapidly dissociated at room temperature. To get efficient energy absorption, light has to be confined inside the active material volume. Complete light coupling has to be targeted under a wide range of exposure conditions, with daily and seasonal variation. A wide angular acceptance for incident light is a gain in system efficiency. Optical light confinement is obtained in standard solar cells with various features: reflective layers on the back side, front and back surface texture to enhance optical coupling ([Kray, 2008](#)) and antireflective coating on the front side ([Kang, Ryu, Upadhyaya, & Rohatgi, 2011](#)).

The second step in PV conversion is charge carriers' collection, which is globally described in [Figure 15.1](#). Photogenerated electrons and holes are not in strong interaction, so they can diffuse independently in a random manner. The active material is not totally pure; silicon contains a certain quantity of chemical impurities and crystalline irregularities. During diffusion, the free carrier is interacting with all these defects and there is a finite probability that the carrier is recombined. This probability is expressed as a carrier lifetime in the doped bulk material. To be able to create a current, the PV device is made of two regions to separate photogenerated electrons and holes before they recombine. One region is electron rich and attracts holes as

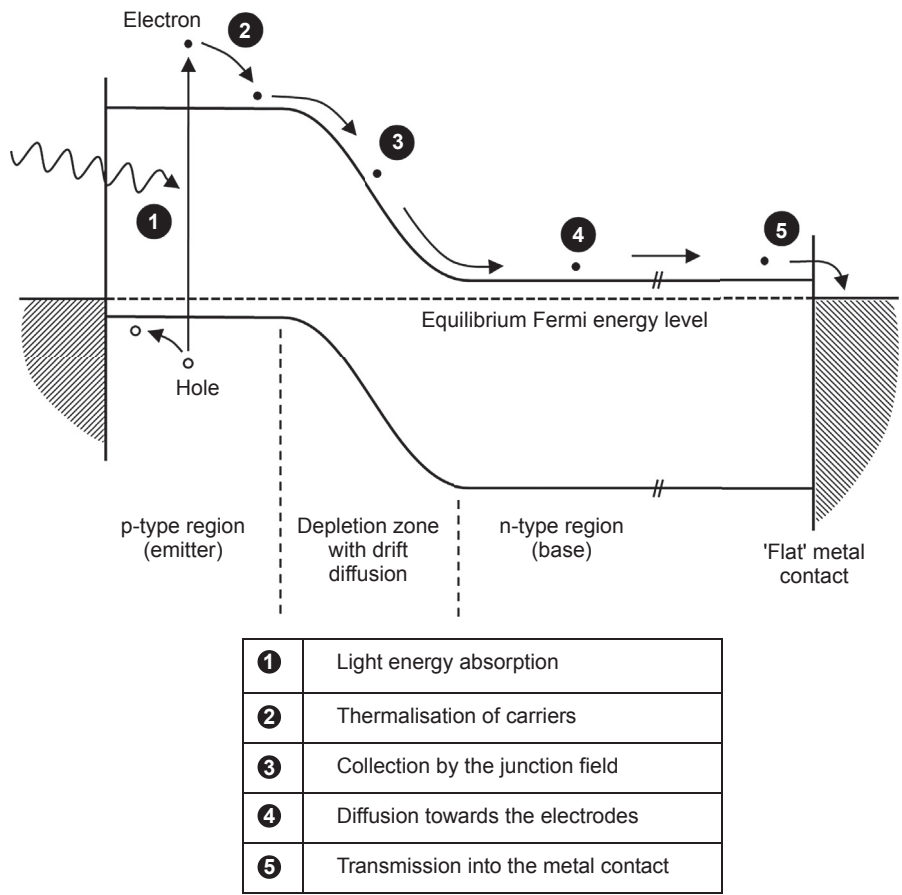


Figure 15.1 Basic principle of photovoltaic conversion showing photon absorption and charge carrier evolution in the energy band diagram of a p–n junction with metal contacts.

minority carriers, and vice versa. The semiconductor material is generally doped with impurity ions to generate n-type and p-type regions. Doping impurity concentration impacts the energy band structure of the semiconductor material. The built-in voltage between the two regions induces an electrostatic intrinsic field in the vicinity of the interface between p-type and n-type regions. At room temperature, majority and minority carriers cross the junction continuously to form the saturation current of the p–n junction. The built-in field captures and pulls apart the minority carriers. The mobility of the carrier (especially minority carrier), the electronic properties of the bulk material and the dimension of the device control the transit of the carrier through the solar cell.

The third step in the PV conversion process is the carrier transit into the metallic contacts. The conductor material, either a metal or a strongly degenerated semiconductor, can be modelled by a free carrier's gas and a single energy level.

The conductor/semiconductor interface is subject to recombination and energy band curvature. The conductor metal is chosen with proper characteristics to reduce the energy barrier height. Finally, the collected electrons and holes travel in the metal finger or plain sheet towards the user electrical load.

15.2.2 *State-of-the-art light management in PV cells*

We focus on the fabrication of the PV solar cell, starting with an available wafer and ending with a single device to be assembled in a larger module. The fabrication of a standard cell is a rather simple process flow with only a few steps: treatment of the wafer surfaces; building the emitter of the p–n junction; deposition of surface coatings (defect passivation, carrier collection); front and back side metallisation, with subsequent contact forming; and etching away possible electrical shunts in the final device. In thin film solar cells, fabrication starts with a passive large substrate that is the size of the final product. All functional layers are deposited on the substrate and scribed to separate subcells electrically connected.

In silicon wafer-based solar cells, the front side is engineered with two optical functions: texturisation through a dry or wet etch process and antireflective coating. Alkaline etching of crystalline silicon reveals a pyramidal geometry in the micron range dimension. This tetrahedral shape leads to a drastic lowering of front optical reflection (Cheng et al., 2012). Other processes have been studied to obtain various geometry of the solar cell front surface: laser ablation, plasma etch, acid wet etch, hard masks, etc. A thin antireflective and passivation film completes the device. Thin film solar cells also use a textured surface to reduce light reflection. The thickness of each layer can be optimised to provide high antireflective global performance. All layers can be adapted to simultaneously provide multiple functions, optical and electrical, to the device.

More advanced concepts are evaluated for optical performance: multiple layers antireflective stack (Zhao & Green, 1991), diffraction gratings optical structures (Haase & Stiebig, 2006) or photonics layers based on plasmonic effects (Pillai, Catchpole, Trupke, & Green, 2007). Electromagnetic field simulation is mandatory to optimise absorption in very thin devices with absorber thickness in the range of 10–100 nanometres as for organic solar cells (Duche et al., 2009). New PV cell designs include advanced concepts issued from photonic and nanotechnology developments.

15.2.3 *Electrical design in standard PV components*

For wafer-based solar cells, the p–n junction device (Figure 15.2) is usually obtained with a dissymmetric design – a rather thick bulk base and a thin emitter. For thin film solar cells, depending on the material used, both regions are similar in thickness.

Industrial homojunction cells are obtained with a thermal diffusion of a doping impurity inside the silicon wafer. The emitter is formed with an excess of said impurity with respect to initial wafer doping level. Base and emitter can be made of two different materials in case of a heterojunction such as boron-doped amorphous silicon deposited on phosphorous-doped crystalline silicon (De Wolf, 2012).

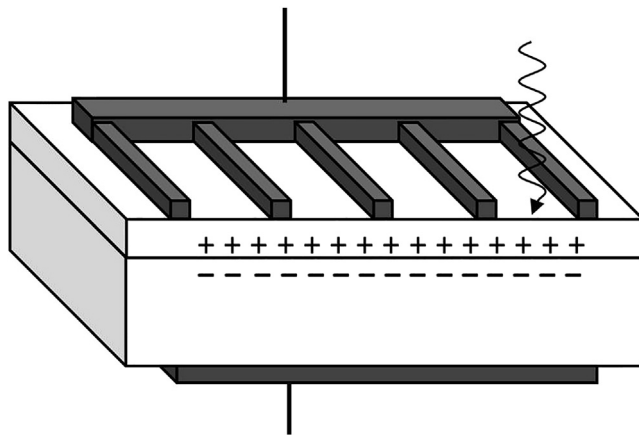


Figure 15.2 Schematics of a photovoltaic device based on the junction of two doped zones, respectively, n and p.

The interface between both regions has to be properly passivated to prevent carrier recombination. A Schottky diode or a metal/insulator/semiconductor (MIS) device also allows the carrier separation and collection, as in historical studies (Green & Godfrey, 1976). This structure appears to be very simple and attractive for specific materials and for nanostructured materials. It is less favourable due to the presence of defects at the interface between metal and semiconductor, light transmission with a front metal layer or tunnelling through the insulator layer.

Light energy is concentrated near the front surface of the solar cell. The emitter of a wafer-based diode is generally set close to this area to avoid loss in the carrier transit through the cell. The carriers move laterally to the closest finger of the metal grid. Recombination occurs due to the emitter's high level of impurities and to the proximity of the surface defects. A passivation layer is needed to annihilate this surface defect as much as possible, either by neutralising each dangling bond or by creating an electrical field effect to push the carriers away from the surface (Aberle, 2001). The emitter can be set on the back surface of the solar cell if a bulk material with a high-level lifetime is used (Terakawa & Asaumi, 2006).

Finally, the carriers transfer to metallic or oxides conductors. Transparent conductive oxides (TCO) are used in some specific designs and thin film solar panels (Perkins & Ginley, 2009). Such materials are mandatory to collect the carriers as close as possible to the region of high photogeneration in case this region presents a huge amount of recombination or a high resistivity. The TCO layer ensures transit to the metal electrodes with minimised loss. For homojunction silicon cells, the metal is directly deposited on the passivation layer and annealed to achieve good contact with low resistance. After metal deposition, solar cells are assembled in series-connected strings to build a solar panel with convenient electrical performance in terms of peak current and voltage. Several strings are then set and connected on the back sheet of the module.

15.2.4 Roadmap for low cost and high efficiency

There are basically two ways to lower the cost of PV energy: reduce the PV device production cost; produce more power with the same device, that is to raise the conversion efficiency to a higher level. Reducing the production cost is a generic concern in the industry. It allows to increase margin and to deploy the product on new markets. Looking for better efficiency usually needs the help of research and development. In both approaches, nanotechnologies can be useful.

Analyses are regularly carried out to establish the limiting factors of PV energy conversion and Table 15.1 shows these limitations (Wolf, 1960). Research-and-development efforts contribute to addressing each of these limitations within some reasonable cost context. PV researchers are looking for an application for these new concepts to address PV efficiency limitations (see Table 15.1).

Historically, PV high-end products were designed for a very specific application: aerospace, which allows the use of expensive devices for spaceship energy supply. Such solar cells show best-ever performance with conversion efficiency above 44% (Green Emery, Hishikawa, Warta, & Dunlop, 2014). These solar cells are a combination of several semiconductor materials to enhance the absorption range over the full solar spectrum, each material being complementary to the others. Different thin film subcells

Table 15.1 Loss factors for an efficient photovoltaic solar cell

Loss factor	Description
Incomplete absorption	Incident light is not completely transmitted into the active material. Light is not completely absorbed in the material with finite thickness and spectral absorption coefficient.
Quantum loss	The semiconductor active material presents an energy bandgap that acts as high-pass filter: photons with low energy are not absorbed. In-parallel photons with a high energy are absorbed, but the energy excess above the gap value is lost in thermalisation.
Collection losses	Carriers have finite lifetime and mobility: a part of the population is recombined before reaching the junction or the electrodes.
Voltage drop and saturation current	The device shows intrinsic loss due to the characteristics of the active material and design. The open-circuit voltage is less than energy bandgap due to doping and temperature on energy level population (Fermi levels). Saturation current induced by the electric field generated at the junction interface decreases the photocurrent.
Resistive losses	Loss due to the serial resistance in solar cell metal electrodes and/or conductive layers (TCO).

are electrically connected to bring a higher extracted power (as multijunction device architecture). III–V semiconductors are used as gallium arsenide (GaAs) or indium phosphide (InP) whose properties and technologies are well known. Their associated ternary and quaternary alloys are engineered to obtain a perfect assembly of three or more material compositions with suitable properties in terms of crystalline quality, light absorption and electrical current balance. These solar cells are obtained in small volume, and they can be used with an optical system to track and focus solar light. Despite the complexity of the use of such materials and cells, III–V multijunctions are highly suitable for high-performance PV cells. Nevertheless, a strong evolution in design and process would benefit the deployment of this technology. Recently, single-junction GaAs thin film solar cell transferred on a low cost substrate demonstrated an interesting perspective (Bauhuis, Mulder, Haverkamp, & Huijben Schermer, 2009). Multijunction concept is also applied with polymer or silicon cells introducing silicon/germanium compound or various crystallised forms of silicon (Yang, Yan, & Guha, 2005).

As in microelectronics, the PV industry looks to unite its development and activities in a global technology roadmap (Green, 2001). The concept of device generation was proposed with a tentative schedule. The definition is founded on cost reduction and conversion efficiency evolution. The first generation was wafer-based silicon solar cells, the second generation thin films and third generation new coming technologies. Technological breakthrough was supposed to separate the different generations. The actors of first generation solar cells are still very active nowadays and both wafer-based and thin films technologies are present together on the market, with a favourable share to wafer-based silicon cells. Historic multicrystalline wafers still exist and show a global performance limited by grain boundaries and multiple crystal orientations. Second generation cells are based on promising materials, apart from amorphous silicon films. Despite multijunction architecture, amorphous silicon technology has considerably decreased in the market perspectives. Cadmium telluride technology has been shown to be very attractive due to a simple and low-cost deposition process, a secured material supply chain and a better conversion efficiency (Gloeckler, Sankin, & Zhao, 2013). Another encouraging material is now available: a chalcogenide alloy of copper–indium–gallium–selenium ($\text{Cu In}_x \text{Ga}_{(1-x)} \text{Se}_2$ or CIGS). This material has been derived from II–VI compounds; laboratories have tried to find a synthesis method that would be suitable for mass production. High conversion efficiency in the 20% range has been shown with microns-thick layers (Schock, 2012). Third generation is not mature and is still in consolidation phase: a lot of new designs and processes have been studied and are candidates for third-generation high-efficiency and low-cost solar cells. Among all these innovative opportunities (Gupta, Alapatt, Podila, Singh, & Poole, 2009), we find nanocomposite materials, nanoscale photonic layers, new processes directly derived from nanotechnologies or bio-inspired architectures.

New players with strong backgrounds in microelectronics technology and nanotechnology are trying to set up in the PV market with high-end products with high conversion efficiency and tightly focussed manufacturing tools. Their backgrounds and their existing facilities allow them to introduce new technologies in fabrication process flow. In the same way, some industries have a strong capacity in design, even design at the nanometre scale. New physical properties arising from nanomaterials have to be taken into account.

New concepts for components probably have to be worked out with powerful design tools, or at least realistic simulations and modelling tools. Considering these contexts at research and industrial levels, nanowires may have a possible future in PV devices.

15.3 Nanowire concept in photovoltaic solar cells

15.3.1 *Expected enhancement of light absorption*

The introduction of nanotechnologies or nanostructures in PV devices is valuable if it allows overcoming one of several cited efficiency limitations. Concerning light confinement, is nanoscale structuration capable of enhancing absorption efficiency? Concerning quantum loss and carrier collection, are nano-objects usable for bandgap engineering without degrading material electrical or thermal performance? Can we better control carrier recombination and how do we achieve doping efficiency? The new properties of nanostructured matter will enable breakthroughs in PV devices towards high conversion efficiency, lower costs for energy production and more attractiveness on the market.

Academic researchers have promoted new physical properties linked to nanometre scale. As light propagation is strongly affected by the structured surfaces of PV solar cells, looking into structuration at wavelength or subwavelength dimensions is a promise for PV efficiency increase. Light propagation in nanostructured media obeys different rules than standard refraction, reflection and transmission laws. This effect has been well known for a long time with one-dimensional array with pitches in the range of wavelength — light is diffracted according to the grating geometrical characteristics and material optical constant. Light diffraction depends also on wavelength and one can produce spectral filters with such optical components. By using the same principle in two- or three-dimensional structures, optical smart coupling can be achieved on a certain range of wavelength and range of acceptance angle. Such photonic crystals are studied for light propagation in optical fibre with very low loss. This concept is based on specific 3D-interferential structures designed on surfaces. Various optical behaviours can be obtained, especially enhanced antireflection coefficient. Such a 2D-photonic layer can be obtained by the controlled growth of localised silicon nanowires. Some groups have shown reflectance-specific resonance and very low reflection coefficient of light with such structures (Muskens, Gomez Rivas, Algra, Bakkers, & Lagendijk, 2008). Light is an electromagnetic wave that can resonate with the propagation environment if properly structured. Simulation has shown that absorption efficiency in nanowire arrays is nicely compared to thin film (Li, Yu, & Li, 2012). Figure 15.3 illustrates the basic principle for a nanowire array interaction with light spectrum. Typical pitches of such a wire array would be in the range of 0.1–1 μm . A concern is to design the structure to obtain antireflection on a broad wavelength spectrum together with a wide acceptance angle range (Xie, Oh, & Shen, 2011). Defining the global symmetry of the nanowire array as a regular network will drive the light ray spatial diffusion (Kelzenberg, 2010). Another issue with a thin device will be to ensure enough confinement to allow efficient absorption inside the PV converter active material.

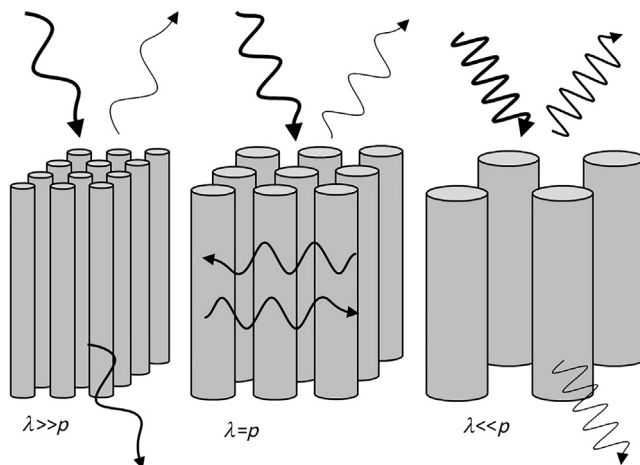


Figure 15.3 Processes of light diffraction on a 2D-structured photonic layer, depending on wavelength λ (lambda) and grating pitch p . Thickness of the waves gives a rough indication of the amount of reflected, transmitted or scattered light.

Electromagnetic field distribution is simulated in the nanowire array with finite difference time domain methodology (Lin & Povinelli, 2009). Figure 15.4 represents an image of superimposed field distribution for an array of silicon nanowires. The design of wire arrays for optical diffraction is at first driven by the pitch dimension, in both directions of the array plan. The reflection and transmission Fresnel coefficients are affected in first order by the filling factor or the size-to-pitch ratio. It has also been shown that silicon nanocone arrays show enhanced absorption over nanowire array and thin film (Zhu et al., 2009). Nanocones or nanopyramid arrays allow a more complete optimisation of light harnessing, either as an active PV layer (Hua, Wang, Yu, Leu, & Fan, 2013) or as a top antireflective coating deposited on a thin film solar cell (Li et al., 2010). The shape of wires has an effect on light absorption in the device, as enlarged foot (Diedenhofen, Janssen, Grzela, Bakkers, & Gomez Rivas, 2011). It will control the high frequency behaviour of the array that is basically derived from a Fourier transform. There is current interest to design specific section and height profile of the wire. Usually, all wires are of the same shape in an array, but a geometrical harmonic could be introduced with a subgroup of individuated wires. In a wider way, geometry can be modified along the height of the wire and we can even go to a full 3D design with wires that shrink and swell along their height (growth temperature, process gases or catalyst choice). Simulation offers the possibility to provide results with a cylinder radius that depends on height – more control is possible on light absorption management, as in a 3D-like metamaterial (Deinega & John, 2012).

15.3.2 Electronic properties and bandgap engineering

GaAs multijunction technology showed highest efficiency is achieved with an assembly of multiple materials with properly designed bandgap energy values. This is possible with ternary or quaternary semiconductor compounds, as III–V or II–VI

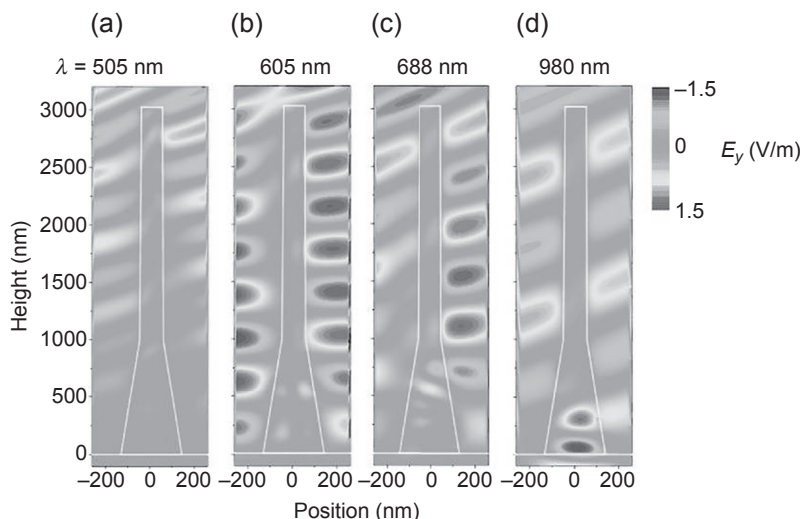


Figure 15.4 Simulation of electromagnetic field amplitude in a section plan of a nanowire array with 40° incidence angle at various wavelengths.

Reprinted with permission from Dienenhofen, S. L., Janssen, O. T. A., Grzela, G., Bakkers, E. P. A. M., & Gomez Rivas, J. (2011). Strong geometrical dependence of the absorption of light in arrays of semiconductor nanowires. *ACS Nano*, 5, 2316–2323. Copyright 2011, American Chemical Society. <http://pubs.acs.org/doi/full/10.1021/nn103596n>.

family. Materials composition directly affects the gap. But the most available material in PV industry is silicon, an element from column IV. In this column, we have very few semiconductor materials that would allow the composition of a crystalline alloy to vary the bandgap. Germanium (Ge) is a viable candidate even if tin (Sn) could be envisaged. Germanium bandgap (0.7 eV) is close to silicon bandgap (1.1 eV) and the achievable range for SiGe alloy is not broad enough to propose a valuable coverage of solar spectrum. Nonetheless, it would be possible to use amorphous materials, but the results are deceiving: the gain in light absorption is lost in carrier transport. Tandem or three-junction cells reach efficiency values well above 10% (Yang, Banerjee, & Guha, 1997). There is no clear possibility to design an efficient multijunction device with crystalline silicon PV technology.

Researchers in nanoscale physics have shown with simulation and experimental evidence that quantum confinement affects the bandgap value for semiconductor nanocomposite materials (Delley & Steigmeier, 1995). These materials could be semiconductor nanoparticles in insulating encapsulating material for 3D quantum confinement or in the same way nanowires for 2D confinement (Read et al., 1992). Nanostructures are then really small – diameter in the nanometre range. Typical bandgap energy excursion is significant with nanostructures smaller than 3 nm, as stated with the curves of Figure 15.5. Calculation and experimental results confirm that silicon nanostructures show a blue-shifted energy bandgap depending on their geometrical nanoscale characteristics (Ma, 2003). This property theoretically

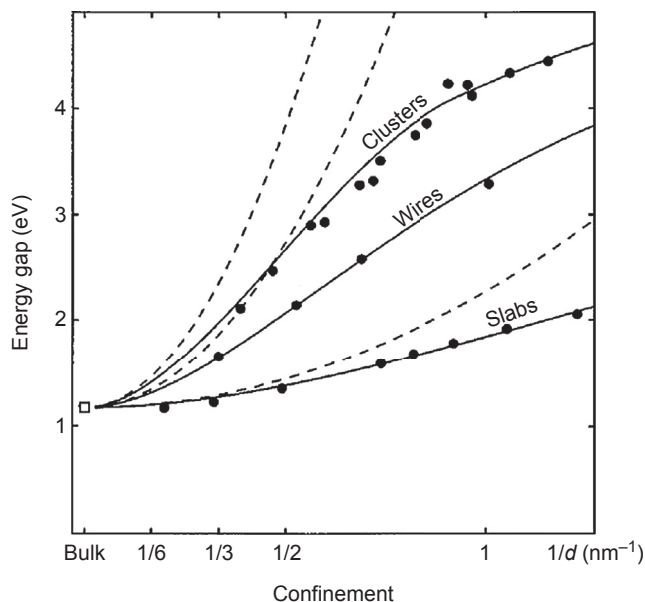


Figure 15.5 Energy gap versus quantum confinement parameter $1/d$, d being the characteristic size of clusters, nanowire or slabs obtained from various models.

Reprinted with permission from Delley, B., & Steigmeier, E. F. (1995). Size dependence of band gaps in silicon nanostructures. *Applied Physics Letters*, 67, 2370–2372. Copyright 1995, AIP Publishing LLC. <http://scitation.aip.org/content/aip/journal/apl/67/16/10.1063/1.114348>.

allows the design of all-silicon multijunction solar cells, with conversion efficiency value expected to reach the level of III–V solar cells. Such a tandem device could be, for example, an array of nanoscale wires grown on a silicon substrate. A first subcell would be the substrate itself, and the second subcell the array of nanowires. A third cell could even be designed with smaller nanowires on top of the first array of nanowires. The difficulty here is to obtain wires with so small diameter – quantum confinement is obtained with less than 3 nm for silicon nanowires. Then the embedding environment has to be controlled; Ma showed that adsorbed atoms at the crystalline interface of the wire can impact the electronic properties. Bandgap control is achieved at laboratory level on a few well-controlled nanowires, as presented in Figure 15.6. But we are far from practical application of quantum nanowires; the first question to consider would be about the behaviour of a collection of an assembly of such parallel wires.

Nanowire geometry affects the electronic property of the semiconductor material. Nanostructured composite materials are usually semiconducting nano-objects embedded in a dielectric environment, as silicon nanoclusters in silica. We assume such a nanocomposite will be a perfect light absorber by design, that is there is no interaction between optical and electronic properties requirement, respectively, 100 and 1 nm lateral resolution. The nanocomposite material also needs to meet global

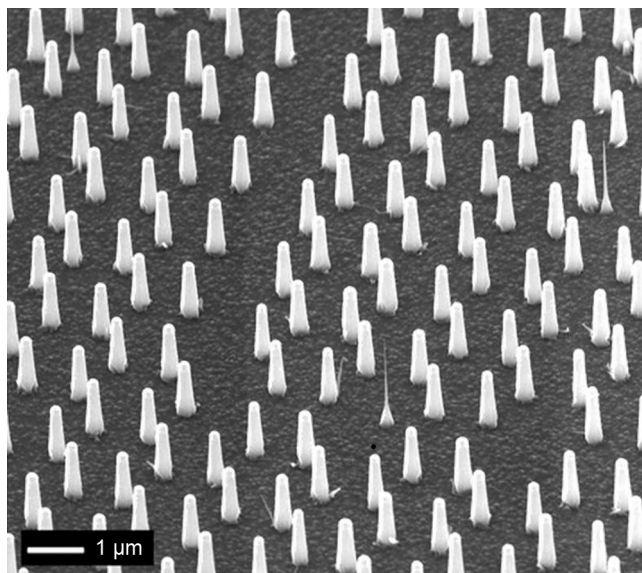


Figure 15.6 Regular array of InP wire 300 nm in diameter obtained with nano-imprint gold catalyst, small wires being grown from parasitic catalyst.

Reprinted with permission from Martenson, T., Carlberg, P., Borgström, M., Montelius, L., Seifert, W., & Samuelson, L. (2004). Nanowire arrays defined by nanoimprint lithography. *Nano Letters*, 4, 699–702. Copyright 2004, American Chemical Society. <http://pubs.acs.org/doi/full/10.1021/nl035100s>.

electrical requirements, such as high conductivity and low recombination rate. This material is something between a perfect insulator (silica) and a bad conductor (intrinsic silicon). In bulk semiconductors, conductivity is achieved and controlled with doping impurity incorporated in the crystalline network. The impurity atom has either an electron in excess or a vacancy with respect to the host material (like boron or phosphorus in silicon). If we transpose into 3D-nanocomposite material, the excess carrier is probably confined in one particle — it does not contribute to the conductivity without a nonnegligible amount of energy (Diarra, Niquet, Delerue, & Allan, 2007). Other conduction mechanisms are involved as tunneling or hopping. These mechanisms can degrade carrier transfer efficiency. By using nanowires, we should avoid this issue by having a possible conductivity along the wire (Storm et al., 2012). A nanowire array possibly presents the unique feature to show quantum confinement in the array plane and free carrier transport in the wire direction. Decoupling longitudinal and lateral effects is a general interesting property of wires, even for larger diameters where no quantum confinement occurs.

But at quantum dimensions, electron and holes propagation are driven by wave function and possible resonance and interference within the wire or with external magnetic or electrostatic fields. Modelling and simulation have predicted that single nanoscale cylinders' conductance could show some quantification effects,

especially at very low temperatures (Kramer, Masek, Spicka, & Velicky, 1990). The effect of periphery and core can be distinguished. Experimental results in the microelectronics domain showed such effects (Nakajima et al., 1994). Coupling between nanowires is also observed between several parallel nanowires, so the behaviour of a full array will include individual properties as well as global characteristics that diverge from individual properties. Depending on experimental conditions and nanowire implementation in the final device, Ohm's law could still be completely valid even for nanowires (Weber et al., 2012).

15.3.3 A solution for material mechanical properties

There is a long experience in the PV domain on film deposition to build solar cells on substrate with square meter size. Such technology has low production costs, mainly due to the direct manufacturing of large products and high-absorptive active materials (amorphous silicon or II–VI polycrystalline compounds). But material quality is not as high as for crystalline wafer and conversion efficiency is capped by poor electronic global characteristics. On the contrary, very efficient materials are obtained by deposition process on a small surface, as III–V compounds. These crystalline materials only grow on high quality substrates like germanium wafers in complex and expensive vacuum deposition systems (metal-organic chemical vapour deposition, MOCVD; or molecular beam epitaxy, MBE). Thin film technology produces either low cost but low performance solar cells or expensive and high efficiency solar components.

Nanowire growth processes offer an alternative to such a dilemma, by allowing good quality heterogeneous structures to be worked out. Crystalline III/V wires are grown on silicon substrate (Krogstrup et al., 2010; Wei et al., 2009) or silicon crystalline wires grown on glass (Sivakov et al., 2009; Stelzner et al., 2008), glass prepared with a TCO coating (Yu, O'Donnell, Alet, & Roca i Cabarrocas, 2010) or an intermediate barrier film. The diameter of wires impacts the crystalline arrangement between cylinder centre axis and edge. The lattice mismatch is dependent on the extension of the interface between both materials. As far as the edge stress does not exceed a limit value, the regular arrangement of atoms is respected. For a limited diameter, a monocrystalline wire is grown on the heterogeneous substrate with no stress relaxation. Then stress will affect the electronic properties of the material at the bottom of the wire. Control of the growth axis also requires additional means. Finally, growing an array of nanowires can be a solution to obtain a crystalline material on a low cost substrate.

The control of the nanostructure permits the optimisation of optical and electrical properties. Less material is needed to obtain a layer with the same properties (a factor of 10). During the deposition, a part of the raw precursors is pumped away from the deposition chamber. The process efficiency for nanowires growth has to be evaluated from this point of view. The deposition speed is also different, so we can have a gain in processing time if we compare a plain layer and a nanowire array with same thickness. High deposition speed results in important cost savings for an industrial nanowires manufacturer.

15.3.4 Tools for nanowire solar cells design

Engineers or researchers have to design the PV device to take advantage of outstanding physical properties of nanowires. The concept of metamaterial and multiscale modelling approach can be used with functional properties defined at intermediate scale. Various possibilities exist depending on the typical size of the nanowire: submicron wires are suitable for optical optimisation and truly nanoscale wires allow electronic properties tailoring.

Optical simulation relies on proven methods and we have stated that numerous research groups have come up with efficient demonstrations (Wen et al., 2011). With semiempirical models, conversion efficiency can be derived (LaPierre, 2011). Researchers sometimes propose design tools or methods for submicron wires (Christesen et al., 2012) that can be applied for various materials as low-grade silicon, for example (Gharghi, 2012). Material simulation is often used by researchers to derive electronic properties: energy band structures, density of state, etc. These properties are derived from lattice structure with infinite volume extension. Nanostructured semiconductors break the hypothesis by showing discontinuities at a characteristic length within atomic distance. Nanoscale patterns act as a modulation of the electronic properties that can result in quantum effects. The effect on various characteristics of the semiconducting metamaterial are then studied, based on the simulation of an assembly of several nano-objects. An energy band diagram can be calculated for the specific cylindrical geometry to find out that energy bandgap can be considered as direct in a single silicon nanowire (Zheng et al., 2005). Simulation tools are specific for a given scale — ab initio calculations for atoms arrangement, to semiempirical models for micron-scale devices. In this latter context, a standard microelectronics software suite can be used to simulate and predict nanowire solar cell performance (Kelzenberg, 2009). A developer's goal is to study numerical paths between ab initio calculation, semiempirical development software tools and PV component. There is definitely a need to extend our knowledge in nanoscale physics to envisage the use of nanocomposite material in a realistic device.

15.4 Nanowire fabrication for photovoltaic devices

15.4.1 Growing nanowires

The growth of nanowires directly on the substrate is used in various panels of deposition tools, chemical vapour deposition (CVD) methods, as well as MBE. The well-known vapour—liquid—solid (VLS) technique is advantageous as demonstrated by Atwater's group (Kayes, Atwater, & Lewis, 2005 or Kelzenberg, 2010). Nanowires epitaxial growth is controlled by a catalyst droplet at mid-level temperature. In CVD methods, the gaseous precursors are cracked in the reactor and dissolved in the liquid catalyst. A frequent choice for the catalyst is gold, but aluminium, tin, copper or other elements can be used. In cases of semiconductor compounds, one element can drive the growth, like gallium for GaAs. As epitaxy happens on the substrate, the

droplet stays in place and a cylinder is formed under the droplet. The height of the wire is controlled by the deposition time, its location and diameter results from the catalyst droplet network. The catalyst is usually removed after growth to prevent undesired effects in the final device (Kendrick, 2010).

To form an array of numerous nanowires, the first step is to pattern the catalyst on the substrate. The simplest way is to demix a thin continuous film with appropriate annealing. A random network of droplets is obtained with dispersed size and uncontrolled location. The size of the catalyst droplet impacts the growth rate of each wire. The length of the wire is generally inversely proportional to the section area, so large wires are shorter. A second solution is the random dispersion of nanoparticles on the substrate, as gold colloids. Particle size can be calibrated, and a random array of wires with the same diameter will be obtained. For small nanoparticles, self-organisation effects may produce a regular pattern. Forces at nanometre scale are strong enough to give catalyst colloids some capabilities to produce a regular planar arrangement (Farrel, Petkov, Morris, & Holmes, 2010). In nanotechnology processes, surface-to-volume ratios are so important that surface forces become strong in regard to volume forces.

To further enhance the control of location and size of catalyst patterns, photolithography is a valuable processes. Microelectronics technology can form very small patterns but at unaffordable cost for PV technology. Nonetheless, some specific techniques can be envisaged because the desired pattern geometry is very simple. Interference deep ultraviolet (UV) photolithography (Kim et al., 2007), nano-imprint or soft techniques (Martenson et al., 2004; Pierret et al., 2010) can be considered to form regular arrays of nanowires as shown in Figure 15.7. Lithography techniques generally allow the formation of a polymer pattern. This pattern is transferred to the catalyst layer. Either the resist mask is formed above the catalyst and is used to etch it, or the catalyst layer is deposited on top of the mask and the mask patterns are removed by a lift-off process. A dense layer of ordered nanospheres can also serve as a mask for catalyst deposition. This cheap process is widely used in combination with various deposition processes (Fuhrmann, Leipner, & Höche, 2005). Copolymers also show self-organisation properties and are used to build patterned layers (Doerk et al., 2011).

It is generally claimed that wires grow perpendicularly to the substrate, but many experimental results show a variety of orientations according to crystalline axis. Silicon nanowires are generally perpendicular to the substrate if this one is $\langle 111 \rangle$ oriented and properly deoxidised. The preparation of the substrate remains a critical step that strongly affects the early nucleation phase as growth initiates (Dick, Deppert, Samuelson, Wallenberg, & Ross, 2008). For wires grown on glass, metal or amorphous layer, orientation is difficult to control. To avoid the growth of disoriented or curved wires, it is possible to build a hard guide layer, as for example a porous alumina layer. Perpendicular wires are grown even on silicon $\langle 100 \rangle$ substrate (Buttard, David, Gentile, Den Hertog, & Baron, 2008).

During the wire growth, it is possible to modulate the diameter of the wire by modifying the process gases. Some specific gases can remove atoms from the catalyst droplets and so reduce the size of the droplets — cones or more complicated forms are grown. Active material can be changed by switching precursor gases — swapping from GaAs to AlAs or more challenging from Si to III/V to form quantum dots

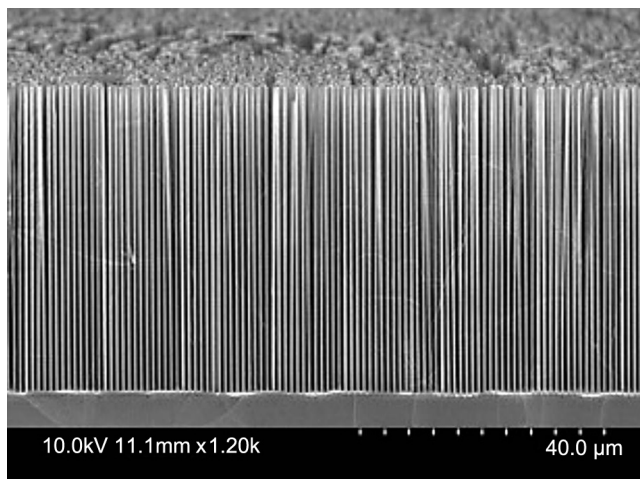


Figure 15.7 SEM image of an array of high-aspect ratio nanowires, obtained with soft lithography and wet etching process.

Reprinted from Li, X. L. (2012). Metal assisted chemical etching for high aspect ratio nanostructures: a review of characteristics and applications in photovoltaics. *Current Opinion in Solid State and Material Science*, 16, 71–81. Copyright 2012, with permission from Elsevier. <http://www.sciencedirect.com/science/article/pii/S1359028611000830>.

(Hocevar et al., 2012). VLS technique enables a wide panel of nano-objects that can greatly enrich PV research activity.

15.4.2 Selective etching of PV material wafers

VLS technique shows limitations, such as facets induced by the crystalline nature of the grown material, catalyst droplets surface diffusion at high density, stacking faults of phase change along the wire, disoriented growth and so forth. The temperature budget required to activate the growth may be responsible for impurity diffusion into the wires or incorporation of catalyst atoms on the cylinder that may affect the performance (as gold on silicon) (Hannon, Kodambaka, Ross, & Tromp, 2006; Oehler, Gentile, Baron, & Ferret, 2009).

Room-temperature chemical etching has been developed as a simple and suitable method to etch pores in silicon and to prepare nanowire arrays (Kolasinski, 2005). The substrate is made of a PV active material or supports a deposited layer of active material. Polished silicon surface can be etched in a one-step wet process. Microstructures will result if the etching solution contains precursors for micromasking of the surface, as aqueous HF-AgNO_3 solution (Li, 2012). This simple process suffers from lack of control of the silver network geometry. It can be enhanced by using silver nanoparticles dispersed in the etch solution. During the etch process, etching occurs below the mask, which acts as an activator (Chartier, Bastide, & Lévy-Clément, 2008). After a given amount of time, a perpendicular and dense array of cylindrical shapes is obtained on the silicon surface as displayed by Li in Figure 15.8. As for VLS growth technique,

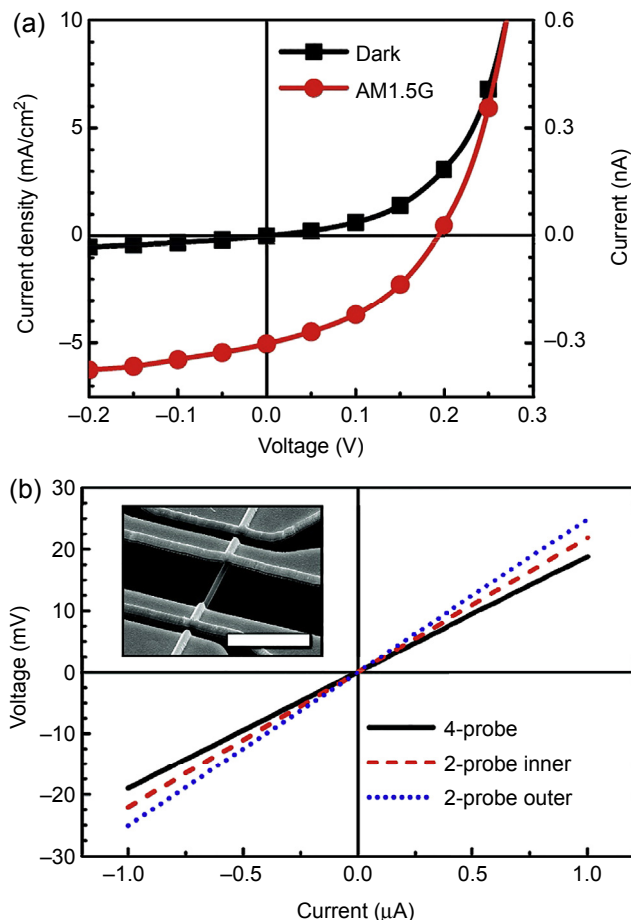


Figure 15.8 Photovoltaic and electrical characteristics of various single-wire devices, diode device with and without illumination (a) and resistor with four contact points (b). Adapted with permission from Kelzenberg, M. D., et al. (2008). Photovoltaic measurements in single-nanowire silicon solar cells. *Nano Letters*, 8, 710–714. Copyright 2008, American Chemical Society. <http://pubs.acs.org/doi/abs/10.1021/nl072622p>.

a metal layer can be patterned on a silicon surface so as to define the wire geometry. The metal layer is obtained with various lithography techniques or with a porous alumina template (Wang et al., 2012). The substrate is then etched in a bath with appropriate reactant concentration and temperature control. The silicon surface in contact with the metal is selectively etched, leaving behind arrays of cylinders. The shape and size of the cylinders are completely defined by the reverse metal pattern. After the etching process step, the catalyst is removed and the nanowire array is dried or prepared for further processing.

Wet etching can be replaced by a dry etching process, as induced coupled plasma etching or reactive ion etching (Garnett & Yang, 2010). The effect of etch technique

can be seen on surface aspect and recombination velocity at the surface. A mask is generated with a simple bead carpet hard deposited by dip coating, but a more complex technique can be envisaged with metal deposition and photolithography techniques to locally preserve the material from etching. Dry etching allowed the highest recorded PV conversion efficiency values in silicon nanowire array (Yoo, Dayeh, Tang, & Picraux, 2013) even with low-grade silicon material (Ghargi, 2012). Dry etching remains an easy technique to set up and offers a large optimisation window with good geometrical control.

15.4.3 *Building a functional device: doping and passivation*

Today the development of growth or etching process is hardly compatible with the fabrication of a quantum device with tailored electronic properties, especially interesting for silicon nanowires. Quantum nanowires with diameter less than 3 nm are difficult to produce and even to observe and characterise. The aggressive surface-to-volume ratio induces bad geometrical stability and preeminent chemical instabilities at the surface. The formation of native or thermal oxide on silicon nanowires can produce a silica shell around a silicon core (Khalilov, Pourtois, van Duin, & Neyts, 2012). Thermal treatment allows an accurate tuning of the core diameter of silicon nanowires and a better control of the curvature and bending of tiny nanowires. Nevertheless, almost all demonstration devices have been realised with rather large nanowires.

Whatever the diameter, consideration should be given to electrical properties, especially to surface carrier recombination velocity. Surface passivation is more and more critical as the surface-to-volume ratio increases. High performing passivation layers are needed, through surface defects annihilation of proximity field effects. An amorphous silicon layer shows good passivation property also for nanowire with a large reduction in surface recombination of nearly two orders of magnitude for small wires (Dan et al., 2011). II–V nanowires usually benefit from a core/shell heterostructure that builds the junction and that provides good surface passivation quality, either GaAs wires with an AlGaAs shell (Tajik, Peng, Kuyanov, & Lapierre, 2011) or InP wires that seem less sensitive to surface recombination than crystalline defects (Joyce et al., 2012). For radial architecture, surface recombination does not show the same impact as for axial architecture.

There is a large benefit to reduce the transit length of carriers in the wire, from their generation inside the active material to the external electrodes. Collecting the carriers on the periphery of cylinders allows defining the transit length to a value close to the radius of the wire. The wire presents a cylindrical core–shell structure with III–V compounds (Colombo, Heiss, Gratzel, & Morral, 2009) or crystalline/amorphous silicon (Tsakalakos et al., 2007). Even for large nanowires with no diffraction effect (above 1 μm diameter), the diffusion length of minority carriers allowed by the wire geometry is advantageous (Kayes, Atwater, & Lewis, 2005). For such broad pillars, light is assumed to propagate from the top of the pillar along the axis and photogenerated carriers. Photogenerated carriers are collected at the periphery, and recombination losses are minimised by the small radius of the wire. This allows efficient PV conversion even with low-quality core material (Gharghi, 2012; Yoon et al., 2010). For plain

film PV devices, the carriers diffuse parallel to incident rays and the diffusion length is roughly equal to the absorption length. A long length provides more light absorption, but a thick layer decreases carrier collection. At any dimension, the nanowire configuration takes advantage of using a radial core-shell design.

The diode architecture used to separate photogenerated charge carriers generally relies on doped semiconductor materials. Nanowire configuration questions the efficiency of doping impurity. Doping can be achieved as for a plain layer by injection of impurity atoms during the growth process. In some specific cases, doping arises from incorporation of atoms from the catalyst in VLS technique. Depending on the size and length of the individual wire, we have a limit in the dopant concentration. This limit is defined by the presence of one impurity in the volume of the nanowire. For wires designed for a photonic crystal structure, we will have 10 to 100 impurity atoms in a single nanowire that would form the base of the diode device (10^{16} to 10^{18} atom/cm³ range). For nanowires that are supposed to show quantum confinement, we will have only a few impurities per wire (10^{19} to 10^{20} atom/cm³ target). Doping regions define the depletion zone of the p-n junction. Its location with respect to wire periphery and substrate geometry is important for device performance (Mallorqui, Eppe, Fan, Demichel, & Fontcuberta i Morral, 2012). Doping level also impacts the Fermi level of energy bands even for nanowires with specific features depending on facets and other nanoscale geometry (Fanetti et al., 2013). Even if we achieve efficient impurity incorporation in the wire crystalline structure, dopant activity is not obvious and carrier excess is not uniform with edge-centre effects (Xie, Hu, Fang, Huang, & Lieber, 2009). Measurement of resistance can assess for the doping efficiencies of experimental devices. Theoretical investigations are needed to evaluate the transport properties of a single nanowire and then the possible resonance between tiny nanowires in a dense array. Innovative architectures for efficient carrier separation and collection as radial heterostructures still need to be worked out, especially with software tools discussed earlier.

15.4.4 Nanotechnology processes integration

To show a progressive understanding of nanowire capacity to produce efficient PV cells, single-wire experiments are very useful. Research laboratories have integrated single wire in small electronic devices. Wires are transferred to a second substrate after their growth or their etching step. With ultrasonic treatment, wires are removed from the original substrate and released in alcoholic solution. Then they are dispersed on the second substrate for further processes. The device is fabricated with the doped shell deposition. One laid-down wire is selected for further individual electrical connections (Kelzenberg et al., 2008). Passivation layers and contacts are patterned on the substrate with microelectronic techniques. A photoresist lift-off process combined with metal deposition formed the electrical contacts at both ends of the wire. As the wire is generally a few microns in length, there is no technical challenge after one wire has been identified on the substrate. The resulting device is especially interesting to study electrical properties of nanowires, including the effect of radial or longitudinal junction, surface defects and passivation layers. Various architecture can be realised and various electrical measurement with or without light can be carried out as shown on

Figure 15.8. The typical characteristic of a PV device is the current–voltage curve under illumination from which the converted energy can be evaluated. For a radial junction, the behaviour of the core and the shell can be precisely evaluated with a proper wiring along the wire (Tian et al., 2007). Various materials can be considered for wires, as silicon, GaAs, InP or CdS in association with more exotic semiconductors (Tang, Huo, Brittnan, Gao, & Yang, 2011). Advanced studies and precise structural characterisation can be realised and innovative materials can be evaluated, for example, graphene for the electrode (Ye et al., 2010).

After characteristics of single wires are investigated, researchers study the behaviour of a whole population of nanowires with millions of features, looking for coupling effects. A first point is to assess is that all wires of a single array are at the same level of performance. A 1-cm² substrate can roughly support 1 billion wires that would be electrically connected in parallel. A small deviation in the growth or etch process can result in a different orientation, diameter and/or length. Optical and electrical characteristics depend on the geometry of the wire, and the deviation can directly impact the optical absorption or open-circuit voltage of the device. A bad uniformity of the thin emitter layer may also result in a shunt of the device. On top of the difficulty of producing a device with architecture that pretends to achieve high conversion efficiency, there is a strong concern in defectivity and process uniformity.

PV devices with homogeneous wire and substrate are easier to handle. The difficulty in the analysis of the results is the proper evaluation of the respective share of wire array and substrate in the photogeneration. As-grown longitudinal and radial junction architectures have been tested with promising results based either on Si or III–V materials, as presented in Table 15.2. The size of the device is a critical gauge, but some very significant results have been published at wafer scale (Jung et al., 2010). Semiconductor technology usually considers flat substrate – deposition on a structured surface needs development. Further processing usually requires encapsulation on the nanowires' array. Gaps between wires are filled with a dielectric or polymer material (Mariani et al., 2011). The filler or host material can be implemented by a wet or a dry deposition process. A sol–gel liquid precursor could be dispensed on the nanowire array. The coating is cured to obtain a solid-state thick layer from which the top of the wires emerge (Perraud et al., 2009). Polishing the composite coating will then smooth the top surface and allow further processing. Concerning electrical properties, the filler is either insulating or conducting depending on the design of the PV cell. A TCO layer can be used for encapsulation to provide a conductor material (Putnam et al., 2010) or to form a Schottky or MIS structure (Bae et al., 2010). If an insulating host is used, contact will be realised at the bottom (i.e. the substrate) and at the top of the wires. If a conductive host is realised, a metal grid is used on top of the front surface. The metal droplet used for the VLS growth (at the top) or for the selective etching (at the bottom) can be used as electrical contacts (Han, 2012). Obtaining a contact on the small section of the wire is not so easy and globally contact resistance varies inversely to diameter of the wire, not only because of the first-order surface, but also because of energy band curvature (Hu, Liu, Ning, Dutton, & Kang, 2008). The voltage versus current curve of such devices shows a high serial resistance characteristic as stated on the curve of Figure 15.9 (Yoo et al., 2013). So as to isolate top and bottom, the process flow includes

Table 15.2 Typical photovoltaic performance of nanowire devices

Technology	Area (mm ²)	Conversion efficiency	Open-circuit voltage (V)	Short-circuit current (mA/cm ²)	Fill factor	Reference
Si dry etch	40	5.3%	0.519	16.8	0.607	Garnett and Yang (2010)
Si dry etch	1	10%	0.44	40	0.38	Yoo et al. (2013)
UMG Si dry etch	25	12.2%	0.591	31.1	0.664	Gharghi, Fathi, Kante, & Sivothaman (2012)
Si VLS	10–20	7.9%	0.498	24.3	0.654	Putnam et al. (2010)
Si VLS on glass/ZnO	3	5.6%	0.76	13	0.57	O Donnell, Yu, Foldyna, & Roca i Cabarrocas (2012)
Si wet etch	78.5 cm ²	7.2%	0.5	20.6	0.698	Jung et al. (2010)
Si wet etch decorated		8.14%	0.55 ^a	25 ^a	0.58 ^a	Peng, Wang, Wu, & Lee (2009)
InP	1	13.8%	0.779	24.6	0.724	Wallentine (2013)
GaAs	0.25	2.54%	0.39	17.6	0.37	Mariani et al. (2011)

^aValues derived from data published in the paper.

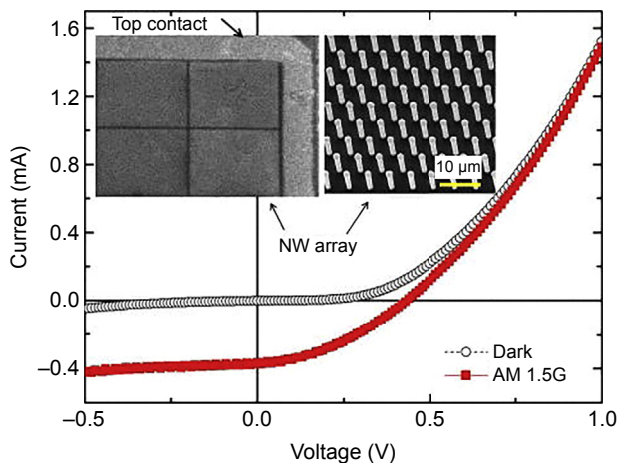


Figure 15.9 Electrical I - V response of a 1-mm^2 array of radial p-i-n wires with top contacts showing 10% conversion efficiency despite high serial resistance and induced low fill factor. Reprinted with permission from Yoo, J., Dayeh, S. A., Tang, W., & Picraux, S. T. (2013) Epitaxial growth of radial Si p-i-n junctions for photovoltaic applications. *Applied Physics Letters*, 102, 093113. Copyright 2013, AIP Publishing LLC. <http://scitation.aip.org/content/aip/journal/apl/102/9/10.1063/1.4794541>.

the deposition of an insulating layer. Holes are opened in this layer and metal is deposited inside these holes. In this way, the bottom of the wire is accessed from the substrate back side (Wallentin, 2013). This latter technique can be used in case of nonselective growth that deposits degraded active material between nanowires. Much more innovative contact structure can be made up, inspired from high-end interdigitated back-contact solar cells. Positive and negative contacts are patterned as a series of alternated rings at the periphery of a neutral wire (Chitambar, Wen, & Maldonado, 2013).

One important challenge is to synthesise nanowires with a high degree of uniformity, especially for heterogeneous devices like III-V wires growth on silicon substrate or silicon wire growth on glass. In GaAs nanowire technology, growth on a $\langle 111 \rangle$ silicon substrate leads to 30% of perpendicular wires (Fortuna & Li, 2010). Disoriented and short wires do not reach the top of the active layer. But further investigation of nanowire growth provides rules for a better control of orientation (Uccelli et al., 2011). A process for silicon wires grown on glass substrate is compatible with silicon thin film facilities. Complete process flow can be defined and integrated to produce wires with good crystalline quality. PV devices could be evaluated with significant performance (O'Donnell, Yu, Foldyna, & Roca i Cabarrocas, 2012).

15.5 Achievements and perspectives

Interest in nanowire technology for PV devices has been very high since 2010. Early single-nanowire devices were produced with simple techniques to demonstrate the

feasibility of junction devices with promising photoresponse. Technology has matured with the fabrication of arrays within significant area. Conversion efficiency has become very significant after analysis of loss factors, namely recombining surface to be passivated and electronic traps inside grown materials (Yuan et al., 2011, Wang, Khan, Lundstrom, & Bermel, 2014). Enhanced and detailed knowledge of growth techniques at nanoscale benefits better control and quality of materials. Experimental results and theoretical considerations seem to agree on the fact that nanowire arrays have the same potential of thin films for PV conversion efficiency, but with much less material consumption. On top of that, this new generation of devices allows for various innovative concepts to raise the efficiency to higher values. New designs should also arise from extended research based on radial architecture, tandem or multi-junction (Wen et al., 2012) or piezoelectric junction induced by strain in III–V structures (Boxberg, Sondergaard, & Xu, 2010). New concepts will arise for PV conversion efficiency breakthrough, as particle decoration placed on wire cylinder. This could result in optical absorption, PV conversion or field effect passivation enhancement (Brittman, Gao, Garnett, & Yang, 2011; Jung, Zhou, Bang, & Lee, 2012; Peng, Wang, Wu, & Lee, 2009). Organic and inorganic active materials build interesting and promising nanocomposites as dye-sensitised or polymer solar devices. These research activities will provide processes and materials suitable for high conversion efficiency, even above the Shockley-Queisser PV classical limit (Krogstrup et al., 2013; Wang et al., 2014)?

Nanocomposite materials usually demand intermediate steps to be usable in a fully integrated industrial process: connections between functional nano-objects, compatible process time and shelf storage lifetime, security issues and so forth. Process integration roadblocks can be envisaged today, for thin film devices or for wafer-based solar cells. A flexible, large PV device can be envisaged as an ultimate thin film cell. To achieve high control of nanomaterial quality on a flexible foil, the nanowire array can be encapsulated in a soft polymer sheet and then peeled off as a nanocomposite self-standing foil (Shiu, Hung, Chao, & Lin, 2009; Kelzenberg, 2010). A very interesting demonstration is also to use nanowires on a wafer-based silicon solar cell that would present a combined pyramidal/nanowire texturisation (Wang et al., 2013). New knowledge from research applied to industry and a new value chain from nano-objects to large PV panels will be developed to make these materials finally available on the PV market.

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Semiconductor nanowire battery electrodes

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16.1 Introduction

Electrical energy storage lies at the heart of human daily life, due to its wide application in cell phones, laptops, cameras, iPads, and so forth (Chu & Majumdar, 2012; Dunn, Kamath, & Tarascon, 2011). Rechargeable batteries are one of the favorable choices taking place of the internal combustion engine by powering electric vehicles (Goodenough & Park, 2013). In addition, there are enormous demands for grid energy storage to balance the distribution and solve the intermittent electricity supply generated by the renewable energy resources, such as solar, wind, and waves (Chu & Majumdar, 2012; Dunn et al., 2011; Goodenough & Park, 2013; Van Noorden, 2014).

Among the electric energy storage techniques, lithium ion batteries (LIBs), introduced by Sony in 1991, now play a major role in consumer life, and they are regarded as the key technology for the further development of hybrid or all-electric cars (Aricò, Bruce, Scrosati, Tarascon, & Van Schalkwijk, 2005; Dunn et al., 2011; Goodenough & Park, 2013; Van Noorden, 2014; Zhang, Uchaker, Candelaria, & Cao, 2013). A battery consists of two electrodes, the anode and the cathode, separated by electrolyte and membrane. In discharging process, the Li^+ ions are extracted from the anode, diffuse through the electrolyte and intercalate into the cathode, while it is opposite in charging process, namely a “rocking chair” battery. The reversible capacity of LIBs is limited by the amount of the exchanged electrons/ions and the material structure stability during the intercalation/deintercalation process (Liu, Li, Ma, & Cheng, 2010). For further achieving higher energy density, the Li–S and Li–air batteries have generated enormous interest all over the world (Bruce, Freunberger, Hardwick, & Tarascon, 2012; Ji, Lee, & Nazar, 2009; Peng, Freunberger, Chen, & Bruce, 2012; Thotiyl et al., 2013). The rechargeable Li–S battery operates by reduction of S at the cathode during discharging, combining with Li to ultimately produce Li_2S with a theoretic capacity of 1675 mAh/g. The Li–air battery is composed of Li anode, porous cathode, and non-aqueous/aqueous electrolyte. At the cathode, O_2 enters the porous cathode, dissolves in the electrolyte within the pores, and is reduced to O_2^{2-} at the electrode surface, forming Li_2O_2 on discharge. The Li_2O_2 is then decomposed on charging. Along with the widespread use of large-format LIBs, the increasing demand for Li chemicals and geographically constrained Li mineral reserves will drive up the prices. In consideration of the larger abundant resources and lower cost of Na compared with Li, Na-based batteries have the potential to meet the large-scale grid energy storage

needs (Cheng, Liang, Tao, & Chen, 2011; Ellis & Nazar, 2012; Liu et al., 2013; Yang et al., 2011).

For various types of batteries, higher specific capacities, shorter charge time, higher rate performance, and longer working life are essential to meet the increasing demands for electrical energy storage devices. The emerging nanoscience and nanotechnology offer a new and revolutionary opportunity to achieve the goals for the above requirements (Barth, Hernandez-Ramirez, Holmes, & Romano-Rodriguez, 2010; Bruce, Scrosati, & Tarascon, 2008; Yang & Tarascon, 2012). During the past three decades, nanomaterials have shown novel physical and chemical properties differing from the bulk counterparts (Bruce et al., 2008; Dasgupta et al., 2014; Kempa, Day, Kim, Park, & Lieber, 2013; Yan, Gargas, & Yang, 2009). Among the various nanostructures, one-dimensional (1D) nanostructures, such as wires, fibers, belts, ribbons, rods, tubes, and scrolls, have been extensively studied because of their interesting and unique electronic, optical, thermal, mechanical, and magnetic properties (Barth et al., 2010; Bruce et al., 2008; Dasgupta et al., 2014; Jiang, Li, Liu, & Huang, 2011; Kempa et al., 2013; Wang & Cao, 2008; Xia et al., 2003; Yan et al., 2009). And in the past two decades, a tremendous amount of progress has been made in this field, greatly promoting the development of high-performance electrochemical energy-storage devices.

16.2 Properties of nanowires for energy storage

Nanomaterials differ from bulk and microsize materials, not only in the scale of their characteristic dimensions but also in other novel physical properties and new possibilities for various technical applications (Dasgupta et al., 2014; Jiang et al., 2011; Kempa et al., 2013; Yan et al., 2009; Zhang, Uchaker, et al., 2013). Reducing the crystal size can shorten the Li ion transport distances; thus the rate of ion insertion/deinsertion is largely increased. Meanwhile, the large surface area of nanomaterials permits a large contact area with the electrolyte and hence a high ion flux across the interface (Goodenough & Park, 2013). Different from other nanostructure materials, the nanowire geometry has been widely studied due to several favorable properties, demonstrating its superiority in battery electrode application. The advantages of nanowires for energy storage are briefly listed below.

- Nanowires offer a direct current pathway to the electrode, improving charge transport compared with particle electrodes (Chan et al., 2008; Liu et al., 2008; Mai et al., 2009; Yang, Gong, et al., 2013).
- The ion diffusion length is greatly shortened, which has the potential to increase the rate performance, because the characteristic time for ions to diffuse through an electrode material (t) depends on the diffusion length (l) and diffusion coefficient (D) according to the relation $t \sim l^2/D$ (Aricò et al., 2005; Hosono, Kudo, Honma, Matsuda, & Zhou, 2009; Honso et al., 2012; Jiang et al., 2011).
- Nanowires provide a high surface area, enabling large electrolyte–electrode contact areas and reducing the charge/discharge time (Barth et al., 2010; Bruce et al., 2008; Xia et al., 2003).

- Nanowires accommodate the volume expansion and restrain the mechanical degradation, enabling long-life cycling (Chan et al., 2008; Meduri, Pendyala, Kumar, Sumanasekera, & Sunkara, 2009; Szczec & Jin, 2011).
- Nanowires are pliable and can be assembled to thin film like papers, making possible flexible applications (Chen et al., 2012; Gwon et al., 2014; Jia et al., 2012).
- Nanowires can directly grow on metal or carbon surfaces as arrays, freestanding and binder-free (Chou, Wang, Chew, Liu, & Dou, 2008; DiLeo et al., 2011; Li, Tan, & Wu, 2006; Yu, Park, et al., 2011).
- Nanowires can act as the building blocks to construct complex and multifunctional architectures, combining the advantages of each subunit (Cui, Yang, Hsu, & Cui, 2009; Mai, Yang, et al., 2011; Xia, Tu, Zhang, Wang, et al., 2012; Zhou, Cheng, et al., 2011).
- Nanowires have the natural geometrical advantage for *in situ* electrochemical probing. With the length over tens of micrometers and diameter around tens of nanometers, single nanowire electrodes can be built to *in situ* investigate the high-resolution structural and electrical evolution without the influence of nonactive materials during battery operation (Huang et al., 2010; Liu & Huang, 2011; Mai, Dong, Xu, & Han, 2010).

16.3 *In situ* probing on single nanowire

The energy density, power density, safety, and cycling stability are the key factors in the applications of energy storage devices. Among them, capacity fading issues pose a critical problem that largely limits the development and optimization of high-performance electrode materials. Thus, the fundamental mechanism of capacity fading and the direct relationship among electrical transport, structure, and electrochemical properties of electrode materials have been considered extremely necessary to be fully understood.

With the development of technology and the progress of experiment design, there is growing interest in developing various *in situ* techniques for energy-storage device studies, such as optical microscopy, transmission electron microscopy (TEM) (Gu et al., 2012; Huang et al., 2010; Karki et al., 2012; Kushima, Huang, & Li, 2012; Kushima et al., 2011; Lee et al., 2013; Liu & Huang, 2011; Liu, Huang, et al., 2011; Liu, Liu, et al., 2012; Liu, Wang, et al., 2012; Mai et al., 2010; McDowell et al., 2013, 2012; Wang, Li, et al., 2012; Zhong et al., 2013), X-ray diffraction (XRD) (Misra et al., 2012), scanning electron microscopy (SEM) (Boles, Sedlmayr, Kraft, & Mönig, 2012), nuclear magnetic resonance (NMR) spectroscopy (Ogata et al., 2014), and Raman spectroscopy (Mai et al., 2010). As electrode for energy storage devices, the nanowires structural evolution can be clearly investigated without the effects from non-active materials during operations. Meanwhile, the nanowire with axial electronic transport properties make it conveniently connected with the metal conductors, compared with other materials such as particles and spheres. These properties allow nanowires to provide a unique platform to investigate the fundamental scientific issues in the field of nanoscience and nanotechnology. The *in situ* single-nanowire electrode studies have provided deeper and more direct insight into the material characteristic change during the charge and discharge process. In this chapter, the main focus is on *in situ* TEM and electrical transport probings.

16.3.1 In situ TEM probing on single nanowire

The *in situ* TEM is a powerful tool and has been widely utilized to provide mechanistic insight into the microstructural degradation of single nanowires during the electrochemical processes because of the high resolution.

Huang et al. (2010) creatively designed a nanoscale electrochemical device inside TEM, which consisted of a single SnO_2 nanowire anode, ionic liquid electrolyte, and a bulk LiCoO_2 cathode (Figure 16.1). Interestingly, the *in situ* observation of the lithiation of the SnO_2 nanowire during electrochemical charging showed that a reaction front propagated progressively along the nanowire, causing the nanowire to swell, elongate, and spiral. This work provides vivid observations of the nanowire electrode operation, demonstrating the mechanical robustness and elasticity boundary conditions of the nanowire geometry, which differs from those of bulk materials. Compared with the sequential lithiation of an SnO_2 nanowire from one end to the other, a modified model designed by Wang et al. (2011) in which the nanowire was soaked into the ionic liquid. The surface of SnO_2 nanowire became rough during the generation of

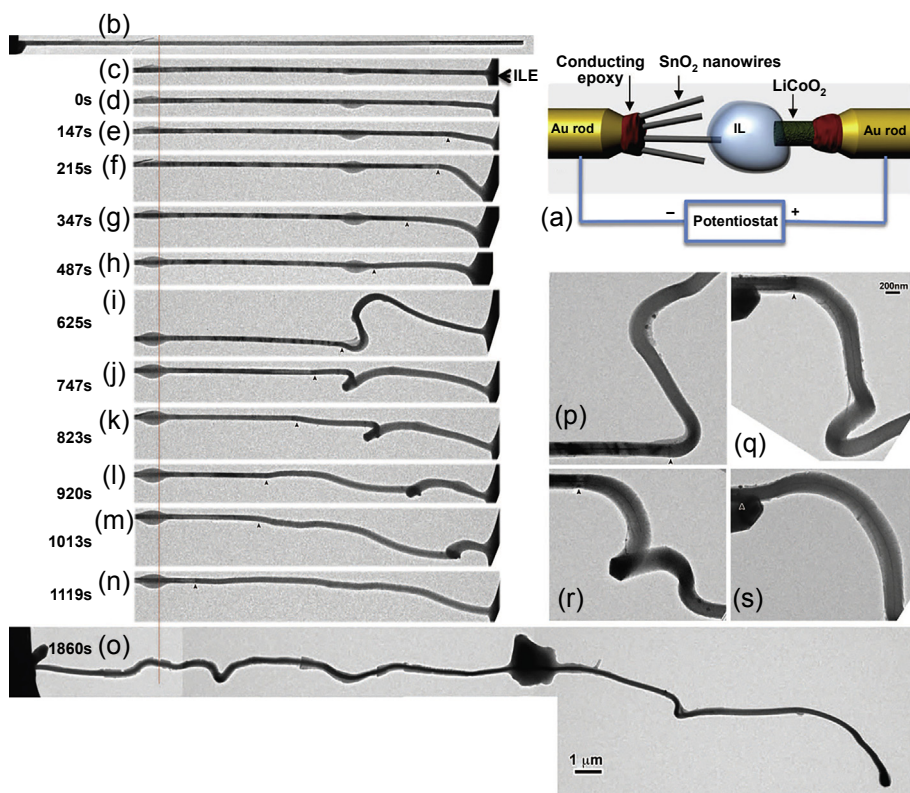


Figure 16.1 (a) Schematic of SnO_2 nanowire electrode. (b–s) Time-lapse structure evolution of a SnO_2 nanowire anode during charging at -3.5 V against a LiCoO_2 cathode. Reprinted with permission from Huang et al. (2010). Copyright 2010 AAAS.

Li_xSn and Li_yO . The lithiation processes of SnO_2 nanowires with different coating materials was further investigated by Zhang et al. (2011). It was found that the charged rate of SnO_2 nanowires was increased about 10 times after coating with copper, carbon, or aluminum. Intriguingly, the radial expansion of the coated nanowires was completely suppressed, as evidenced by the lack of formation of dislocations, resulting in enormously reduced tensile stress at the reaction front. This work demonstrates that nanoengineering the coating enables the simultaneous control of electrical and mechanical behaviors of electrodes, pointing to a promising route for building better LIBs.

Other semiconductor metal oxide nanowires were also undertaken through *in situ* TEM. Kushima et al. (2011) investigated the lithiation process of ZnO nanowires via *in situ* TEM, in which different observations were found. The reaction front did not move continuously in ZnO nanowires. Instead, the leapfrog cracking occurred before the reaction front, and the leapfrog divided the single ZnO nanowire into many segments and lost electrical contact, corresponding to the poor cycling stability of ZnO nanowires. Wang, Tang, et al. (2012) investigated the conversion mechanism of CuO nanowires during lithiation and delithiation. The total volume expansion of the first delithiated nanowire was 165% compared with the pure CuO nanowire. The phase transformation of LiMn_2O_4 nanowires was observed by Lee et al. (2013). The LiMn_2O_4 nanowire was found to be changed into the tetragonal phase at the interface region with electrolyte during the discharge process and restored to cubic phase without any fracture in the charge process. No fracture during the cubic–tetragonal transition make the promising applications of LiMn_2O_4 nanowire cathode for long-life LIBs.

As traditional and significant semiconductor materials, silicon (Si) and germanium (Ge) have high theoretical capacity, but their volume change of semiconductor electrode material upon full lithiation/delithiation is huge (about 281% for $\text{Li}_{15}\text{Si}_4$ and 246% for $\text{Li}_{15}\text{Ge}_4$), resulting in pulverization of the electrode and significant capacity loss of the LIBs. Besides, the details of the alloying reaction process are not clear (Wu & Cui, 2012). The lithiation process of Si and Ge is usually divided into two steps: (1) the crystal silicon is converted to the amorphous alloys of Li_xM ($\text{a-Li}_x\text{M}$, $0 < x < 3.75$, $\text{M} = \text{Si, Ge}$); and (2) the crystallization process occurs from $\text{a-Li}_x\text{M}$ to $\text{c-Li}_{15}\text{M}_4$. Liu, Zheng, et al. (2011) found that the volume expansion of silicon nanowires was anisotropic and the largest and the smallest volumetric change occurred along the $\langle 110 \rangle$ and $\langle 111 \rangle$ direction, respectively, during the lithiation process via *in situ* TEM probing technology. A sharp interface (~ 1 nm thick) between the crystalline silicon and an amorphous Li_xSi alloy was observed by Liu, Wang, et al. (2012). The lithiation kinetics were controlled by the migration of the interface, which occurred through a ledge mechanism involving the lateral movement of ledges on the close-packed $\{111\}$ atomic planes. Such ledge-flow processes produce the amorphous Li_xSi alloy through layer-by-layer peeling of the $\{111\}$ atomic facets, resulting in the orientation-dependent mobility of the interfaces. Different from the Si nanowire, the volume expansion of the Ge nanowire was isotropic, and the Ge nanowire exhibited porous structures after Li was extracted (Liu, Huang, et al., 2011). The nanopores were formed after delithiation, involving the aggregation of vacancies produced by

Li^+ ion extraction, similar to the formation of porous metals in dealloying. Intriguingly, the porous nanowires exhibited fast lithiation/delithiation rates and excellent mechanical robustness, attributing to the high rate of Li^+ ion diffusion and the porous network structure for facile stress relaxation, respectively. These results suggest that developing reversible porous structure in nanowires is a promising strategy to improve energy capacity, rate performance, and cycling stability.

The nanowire structure has been investigated by *in situ* TEM, and also acts as a powerful platform for observing the lithiation processes of the other nanostructures, such as silicon nanoparticles (Gu et al., 2012; McDowell et al., 2012), nanospheres (McDowell et al., 2013), and yolk-shell structures (Liu, Wu, et al., 2012). The silicon nanowire was even used for constructing an Li–air cell model in the *in situ* TEM. The Li_2O_2 supported on the multi-walled carbon nanotube (MWCNT) was contacted with a silicon nanowire and then the electrochemical oxidation process of Li_2O_2 was observed (Zhong et al., 2013). The developments of *in situ* TEM probing reviewed above give the fundamental understanding of the conversion and insertion reaction mechanisms through real-time observation.

16.3.2 *In situ electric transport probing on single nanowire*

The electron conductivity of the semiconductor nanowire is very important for their electrochemical performance, but they will change during the Li^+ ion insertion/deinsertion. Mai's group designed and assembled the all-solid-state single nanowire electrochemical devices in 2010 (Mai et al., 2010). The device contained just one nanowire as either cathode or anode, and used classical materials for counter electrodes and electrolyte (Figure 16.2). The conductance change of vanadium oxide was restored to previous scale upon Li ions deintercalation, indicating reversible structure change after a shallow lithiation process; but the conductance of the Si nanowire decreased for over two orders of magnitude, and this change was permanent. This observation implied permanent structure change, which was further confirmed by Raman mapping of single nanowire anode together with the Raman spectra of highlighted spots at different charge states.

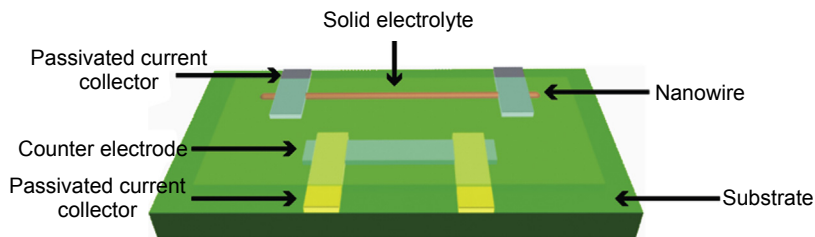


Figure 16.2 Schematic diagram of a single nanowire electrode device design. A single vanadium oxide nanowire or Si nanowire is the working electrode, and HOPG or LiCoO_2 nanofilm is the counter electrode. The electrolyte is the PEO- LiClO_4 -PC-EC polymer. Reprinted with permission from Mai et al. (2010). Copyright 2012 American Chemical Society.

The *in situ* observations have greatly promoted the development of energy storage materials and devices. However, some complex processes are still unclear. To solve this problem, the relationship among electrode material composition, structure, transport properties, charge/discharge state, and electrochemical performance needs to be investigated at the same time. The nanodevices that can be studied at the single nanowire level to reveal the reaction mechanism and the intrinsic reason for fast capacity fading will be a new platform for studying the Li storage process.

16.4 Nanowire structure

Nanowires have been intensively investigated as building components in electrochemical energy storage because they provide short diffusion lengths to ions and electrons, leading to high charge/discharge rates (Barth et al., 2010; Bruce et al., 2008; Dasgupta et al., 2014; Li et al., 2013; Zhang, Uchaker, et al., 2013). Various nanowire structures, such as wires, fibers, belts, ribbons, rods, tubes, and scrolls, have exhibited their own advantages in the energy storage applications. For nanobelts or nanoribbons, their thickness can be reduced to several nanometers or even to the atomic level, which greatly shortens the ion diffusion pathway and increases their rate performance (Yang, Gong, et al., 2013). For nanowires, the ultra-long nanowires will be much more useful compared to short wires for electrical transport, device interconnects, and reinforcing fibers in composites, making possible flexible and wearable applications (Gwon et al., 2014).

Based on *in situ* probeings, it is found that the conductivity decrease of nanowire electrode and structure disorder/destruction caused by phase transformation and volume change during the electrochemical reaction limit the cycle life of the devices. The main strategies of improving the electrochemical performance of electrodes are to concurrently optimize electrical and ionic conductivity, maximize the active material utilization, and minimize strain-induced damage (Mai, Wei, Tian, Zhao, & An, 2014). In addition, side reactions will occur at the electrode–electrolyte interface due to their high surface energy, which will lead to irreversible capacity fading and thus a short cycle life.

As mentioned before, the rational controls during synthesis processes have enabled nanowires to act as powerful building blocks for the bottom-up assembly of complex, composite, and multifunctional nanostructures, which can overcome the drawbacks of nanowires. The corresponding nanowire architectures, including coaxial nanowires, internal porous nanowires, hierarchical nanowires, and nanowire arrays, are summarized next.

16.4.1 Coaxial nanowires

It is really difficult to find a single component that can fulfill most of harsh and often conflicting requirements. Thus, it is always necessary to use more than one component to fabricate composite electrode materials (Cao, Guo, & Wan, 2011). Coaxial nanowires, also known as core–shell nanowires or nanocable, can be defined as a 1D

nanocomposite with different components forming a core/shell structure. Combining the advantages of the core and shell units, the coaxial-structured nanowires are often chosen as an effective strategy to enhance the electrical conductivity, prevent aggregation, improve chemical stability, and buffer the stress of the inner nanoscale active material (Cao et al., 2011; Li et al., 2013; Mai et al., 2014; Wu et al., 2012).

Many approaches have been developed for the synthesis of coaxial nanowires, which include chemical vapor deposition, electrodeposition, template method, wet-chemical method, hydrothermal method, electrospinning, and so forth. Various materials such as active material/carbon, active material/polymer, active material/metal, active material/active material, have been employed as core/shell in coaxial nanowires. Most coaxial nanowires could be classified into (1) active core/conductive shell coaxial nanowires, (2) conductive core/active shell coaxial nanowires, and (3) other coaxial nanowires, as summarized in the next sections.

16.4.1.1 *Active core/conductive shell coaxial nanowires*

Carbon and conductive polymers are usually chosen as the conductive coating layers. The outer carbon layer with uniform and continuous features improve the electrochemical performance in several ways, including maintaining the integrity of inner units and increasing the electronic conductivity of electrodes (Kim & Cho, 2008; Park et al., 2009; Xin, Guo, & Wan, 2012; Zhu, Yu, Gu, Weichert, & Maier, 2011). Also, the outer surface of active material can be protected by the stable coating layer, which leads to the formation of a stable solid–electrolyte interface (SEI) layer and improves the cycling stability.

Coating carbon on the backbone nanowires is one of the most facile and common ways to synthesize coaxial nanowires. Besides, electrospinning is optional technology for the synthesis of coaxial nanowires. Zhu et al. (2011) synthesized highly electroactive carbon-coated single-crystalline LiFePO_4 nanowires via a facile electrospinning following with annealing treatment (Figure 16.3(a)–(c)). The networks of these LiFePO_4/C nanowires showed very short diffusion lengths, leading to high rate performance and cycling capability. In addition, the nanocasting method is another effective strategy for the design of coaxial nanowires. Kim and Cho (2008) used SBA-15 as a template to synthesize mesoporous Si/C core–shell nanowires (Figure 16.3(d) and (e)). The nanowires demonstrated excellent initial charge capacity of 3163 mAh/g at a rate of 0.2 C (600 mA/g) between 1.5 and 0 V, and a capacity retention of 87% after 80 cycles. Moreover, carbon-coated Si nanotubes have been reported to achieve capacities as high as 3000 mAh/g at rates of 5 C (15 A/g) (Park et al., 2009). Therefore, carbon coating can effectively increase conductivity, protect the electrode from direct contact with electrolyte, and provide buffer for the volume change during cycling.

Conductive polymer coating can enhance the electron conductivity of nanowires as well as buffer the volume stress, since the polymers are softer than the hard carbon coating. Liu and Lee (2008) fabricated $\text{MnO}_2/\text{PEDOT}$ coaxial nanowires by a one-step co-electrodeposition method; the MnO_2 core was utilized for its high energy density, while the PEDOT shell was applied for high conductivity, porosity, and flexibility (Figure 16.4(a) and (b)). The PEDOT shell facilitated electrical transport and ion

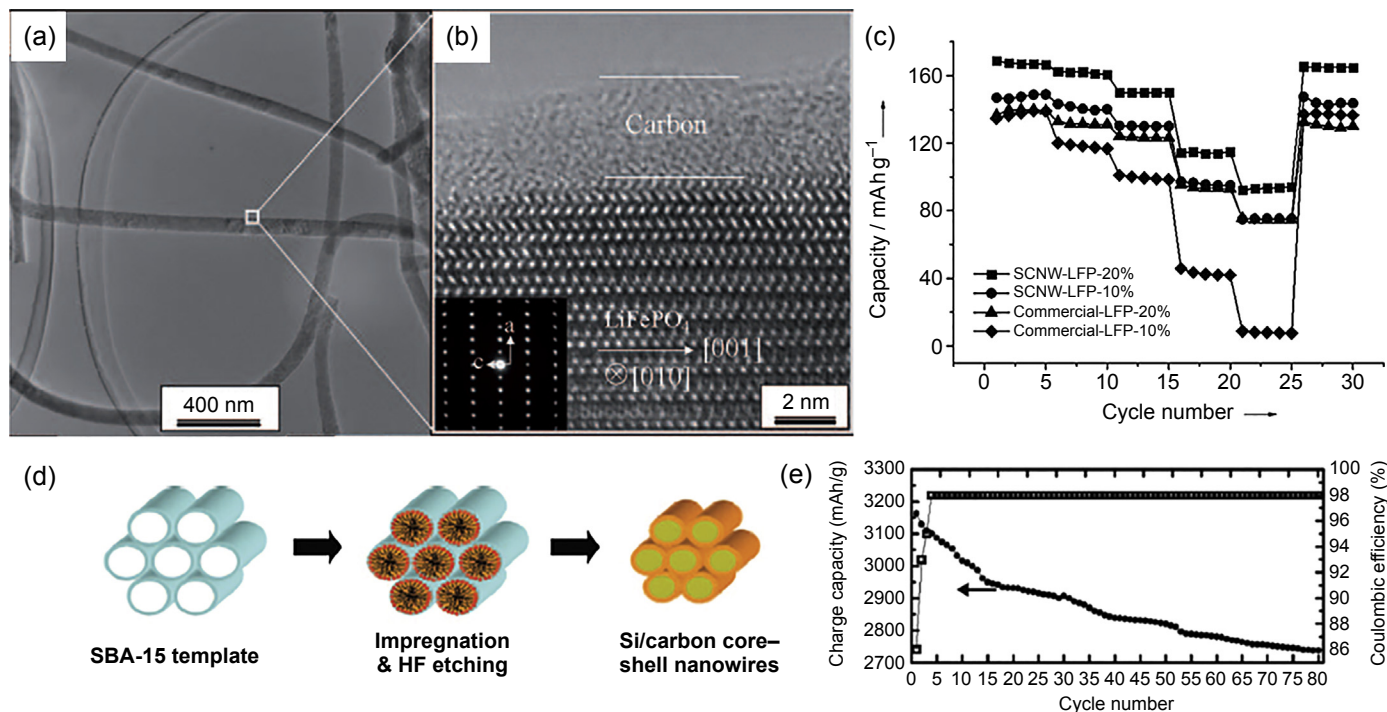


Figure 16.3 (a, b) TEM micrograph of carbon-coated single-crystalline LiFePO₄ nanowires. Inset in (b) is the SAED pattern. (c) Rate performance of carbon-coated single-crystalline LiFePO₄ and commercial LiFePO₄ with 10% and 20% additional conductive carbon. (Reprinted with permission from [Zhu et al. \(2011\)](#). Copyright 2011 John Wiley & Sons, Inc.) (d) Schematic view of the preparation of Si@carbon core-shell nanowires. (e) Plot of charge capacity and coulombic efficiency of the cycle number.

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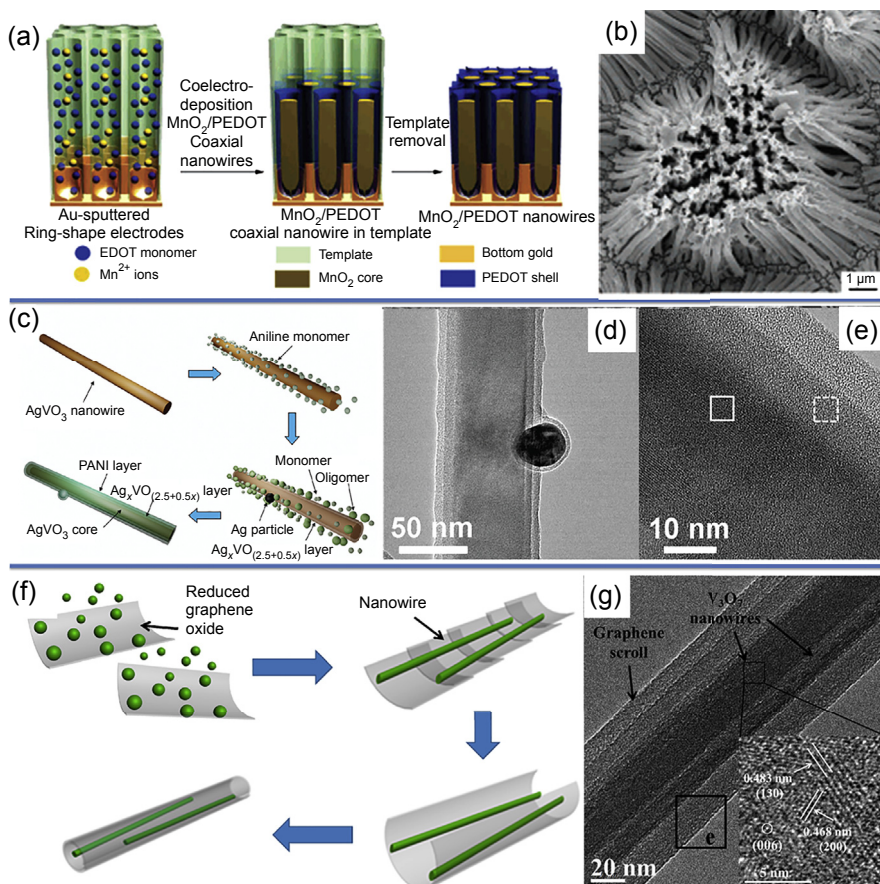


Figure 16.4 (a, b) Schematic illustration of the one-step synthesis of $\text{MnO}_2/\text{PEDOT}$ coaxial nanowires (a) and related SEM image (b). (c–e) Schematic illustration of the *in situ* formation of SVO/PANI triaxial nanowires (c) and related TEM images (d, e). (f, g) Construction processes of nanowire templated grapheme scrolls (f) and TEM images of VGS (the inset gives an HRTEM image of a V_3O_7 nanowire in GSs).

Reprinted with permission from Liu and Lee (2008), Mai, Xu, et al. (2011), and Yan, Wang, et al. (2013). Copyright 2008, 2011, 2013 American Chemical Society.

diffusion into the energy-dense MnO_2 core, and protected the core from structural collapse and breaking. These combined properties resulted in a synergic composite that has very high specific densities. In addition, the polymer can be coated on the backbone nanowires through *in situ* chemical oxidative polymerization. Silver vanadium oxides/polyaniline (SVO/PANI) triaxial nanowires were synthesized via *in situ* chemical oxidative polymerization and interfacial redox reaction based on $\beta\text{-AgVO}_3$ nanowires (Figure 16.4(c)–(e)) (Mai, Xu, et al., 2011). The triaxial nanowires exhibited much higher peak current in CV curve and much lower charge transfer resistance than those of $\beta\text{-AgVO}_3$ nanowires, which indicated faster kinetics and

higher capacity, improving the electrochemical performance obviously. The similar strategy has been utilized for MoO_3 electrode materials to improve discharge/charge capacity and cycling stability (Li, Han, et al., 2011).

Metal coating is another attractive approach to improve electrical transport along the nanowire axis. A biological template method using viruses has also been used to fabricate Au- Co_3O_4 hybrid nanowires (Nam et al., 2006). It was found that the capacity was increased by incorporating Au nanoparticles into the Co_3O_4 nanowires, due to either a catalytic effect from the Au or an improved conductivity of the nanowires.

Remarkably, graphene has motivated intensive efforts to construct graphene-based composite materials, which have been widely used in energy storage and other applications (Li, Wang, et al., 2011; Wang et al., 2010; Yu, Hu, et al., 2011). Most of the active materials were deposited on the surface of the graphene framework or encapsulated as a core in the graphene shell. In fact, graphene can be self-rolled into scrolls, making it theoretically possible to encapsulate nanodroplets or other nanomaterials (Shi, Cheng, Pugno, & Gao, 2010; Zhang, Huang, & Li, 2012). Semihollow vanadium oxides and manganese oxide nanowire core with graphene scroll shell have been constructed through an “oriented assembly” and “self-scroll” strategy (Figure 16.4(f) and(g)) (Yan et al., 2013). This unique structure of the nanowire-templated graphene scroll provided continuous electron and ion transfer channels and space for free volume expansion during cycling, resulting in excellent energy storage capacities and cycling performance. Lithium batteries based on V_3O_7 nanowire-templated graphene scrolls exhibited an optimal performance with specific capacity of 321 mAh/g at 100 mA/g and 87.3% capacity retention after 400 cycles at 2000 mA/g.

16.4.1.2 Conductive core/active shell coaxial nanowires

In conductive core/active shell coaxial nanowires, the core component consists of the electronic conductive material and the shell component consists of the active material. The conductive core act as a small “conductive network” on the nanometer scale, in which the electrons can readily transport (Cao et al., 2011; Xin et al., 2012).

In the context of constructing conductive networks, carbon nanotubes (CNTs) are a favorable choice. As a result of their unique wire morphology, fast electron transmission rate, and robust structure, CNTs can easily form cross-linked conducting networks and serve as the conducting phase (Figure 16.5(a) and (b)) (Cao et al., 2011). Cross-linked conducting networks by coating or loading active materials onto CNTs forming a coaxial architecture can realize the rapid and continual electron/ion transport, which exhibits largely enhanced performance for simply mixing CNTs with actives materials. Many metal oxides have been loaded onto the CNTs to obtain hybrid anode materials with enhanced performance. CNT@ TiO_2 core/porous-sheath coaxial nanocables were synthesized by controlled hydrolysis of tetrabutyl titanate in the presence of CNTs (Figure 16.5(c)) (Cao et al., 2010). The CNT@ TiO_2 nanocables had several structural advantages toward efficient Li storage. On the one hand, the CNT core with exposed ends provided sufficient electrons for the storage of Li in the TiO_2 sheath. On the other hand, the TiO_2 layer effectively prevented the formation

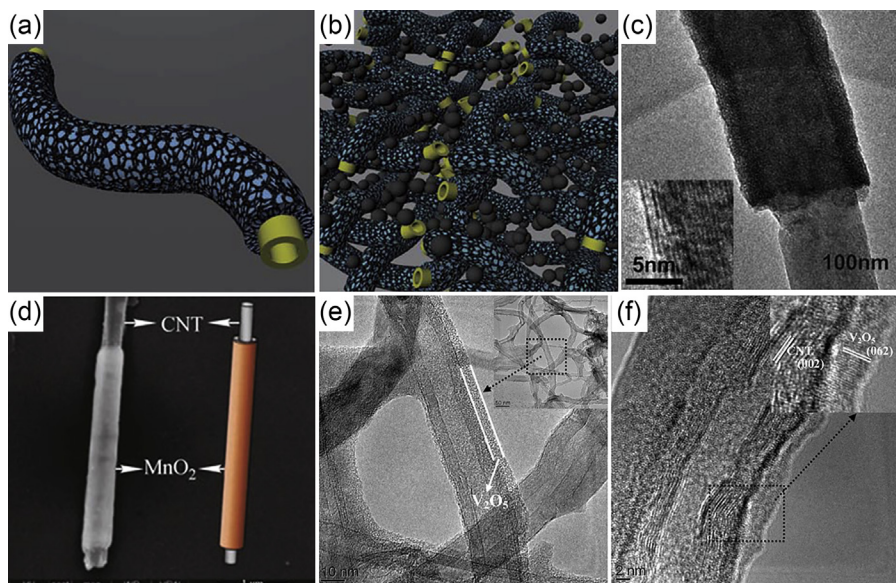


Figure 16.5 (a) Schematic illustration of nanocables with electronically conducting core (yellow) and Li^+ providing nanoporous sheath (blue). (b) Corresponding schematic illustration of the effectively mixed conducting 3D networks formed by the nanocables and carbon black. (c) TEM images of $\text{CNT}@\text{TiO}_2$ nanocables. Inset shows the HRTEM image of the CNT core. (d) SEM image of coaxial $\text{MnO}_2/\text{Carbon}$ nanotube array. (e) TEM image showing the absence of V_2O_5 on CNT surface. (f) High-resolution TEM image showing lattice image of V_2O_5 with CNT lattice.

Reproduced from [Cao et al. \(2011, 2010\)](#), [Reddy et al. \(2009\)](#), and [Sathiya et al. \(2011\)](#). Copyright 2009, 2010, 2011 American Chemical Society.

of a thick and unstable SEI film on the surface of the CNT. The synergic effects of the two components lead to a composite material with high, fast, and stable Li storage. [Reddy, Shaijumon, Gowda, and Ajayan \(2009\)](#) combined simple vacuum infiltration with chemical vapor deposition techniques to prepare MnO_2/CNT hybrid coaxial nanowires. The coaxial hybrid structure formed by the highly conductive CNT core offered enhanced electronic transport to the MnO_2 shell and acted as a buffer to alleviate the volume expansion ([Figure 16.5\(d\)](#)). [Sathiya, Prakash, Ramesha, Tarascon, and Shukla \(2011\)](#) reported a 4–5 nm thin layer of V_2O_5 coated on functionalized multiwalled CNTs by controlled hydrolysis of vanadium alkoxide ([Figure 16.5\(e\) and \(f\)](#)). The resulting $\text{V}_2\text{O}_5/\text{CNT}$ composite was investigated for electrochemical activity with Li ions, and the capacity value showed both faradaic and capacitive (nonfaradaic) contributions. At a high rate (1 C), the capacitive behavior dominated the intercalation, as two-thirds of the overall capacity value out of 2700 C/g was capacitive, while the remaining portion was due to Li ion intercalation. The cumulative high-capacity value was attributed to the unique property of the nano- $\text{V}_2\text{O}_5/\text{CNTs}$ composite, which provided a short diffusion path for Li ions and an easy access to

vanadium redox centers besides the high conductivity of CNTs. The composite architecture exhibited both high power density and high energy density, stressing the benefits of using carbon substrates to design high-performance energy storage electrodes.

Different from CNTs, carbon nanofibers (CNFs) are another favorable choice. Yu's group (Liang, Liu, Qian, & Yu, 2013) developed a simple hydrothermal method for large-yield synthesizing highly functionalized CNFs with abundant hydroxylic and carboxylic groups. The negatively charged carboxylic groups allow the CNFs to capture positively charged metal ions or nanoparticles by electrostatic interactions. And the hydroxylic groups on the CNFs have remarkable reducing ability for *in situ* loading with nanoparticles. These unique abilities of CNFs enable them to serve as secondary templates to generate other 1D nanostructure, especially the coaxial nanowires. Well-defined CNF@MnO and CNF@CoMn₂O₄ coaxial nanocables were facily fabricated through a simple and general two-step strategy involving a polyol process and subsequent thermal annealing treatment (Zhang, Wu, Hoster, & Lou, 2014). These two nanocable electrodes exhibited remarkable Li storage properties in terms of high specific capacity, long cycle life, and superior rate performance, attributed to several advantages of the smart coaxial nanocable configuration.

16.4.1.3 Other coaxial nanowires

The pulverization of electrode material during cycling and an unstable solid-electrolyte interphase may limit the cycle life, especially for the anode materials (Si, Ge, transition metal oxides, etc.). Different from highly conductive or active shells, the stable and robust outer layer is very important.

A double-walled Si–SiO_x nanotube (DWSiNT) anode structure was fabricated by Wu et al. (2012) in which the inner wall was active silicon and the outer wall was confining SiO_x, which allowed Li ions to pass through (Figure 16.6). During lithiation, Li ions penetrated through the outer wall and reacted with the inner silicon wall which will expand inward into the hollow space. During delithiation, the inner surface of the silicon wall shrank back, while the outer wall of the nanotube was stable with the formation of a small amount of SEI layer. The as-synthesized DWSiNT exhibited excellent electrochemical performance, with no significant capacity fading even after 6000 cycles (Figure 16.6(d) and (e)).

For various kind of coaxial nanowires, the coating layer should be permeable to Li ions; thus the lithium ion diffusion in the active materials can be maintained. Moreover, the coating layer needs to be conductive and stable; thus the backbone nanowires can be effectively protected from side reactions with electrolyte and structure degradation. Therefore, better electrochemical performance can be achieved by the rational construction of coaxial nanowires.

16.4.2 Internal porous nanowires

For electrode material, the surface area significantly affects its storage capacity. The surface area of a simple nanowire is limited by its size. However, too thin nanowires tend to self-aggregation owing to increased surface energy. Thus, an approach to

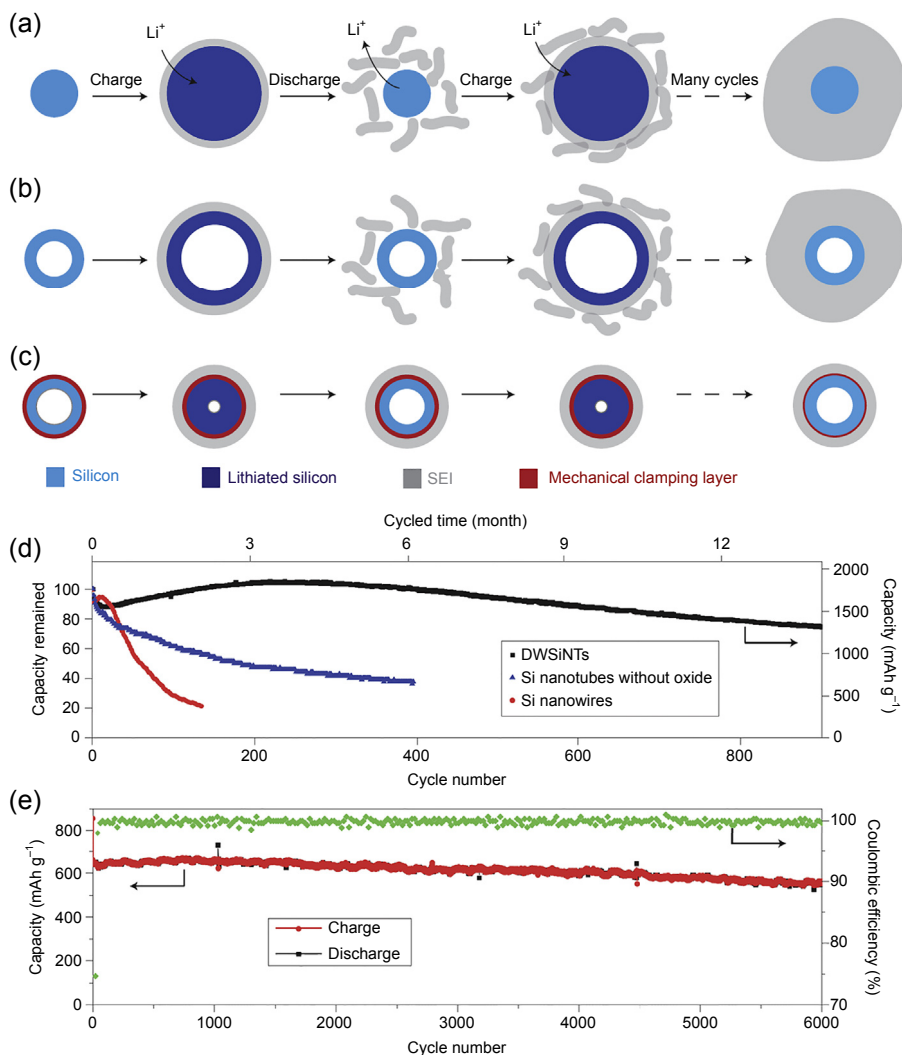


Figure 16.6 Schematic of SEI formation on silicon surfaces. (a) A solid silicon nanowire expands upon lithiation and delithiation, which results in a very thick SEI layer on the outside of the silicon nanowires. (b) Similarly, a thick SEI grows outside the silicon nanotube without a mechanical constraining layer, which also has a varying and unstable interface with the electrolyte. (c) Designing a mechanical constraining layer on the hollow silicon nanotubes can prevent silicon from expanding outside toward the electrolyte during lithiation, with the result that a thin and stable SEI can be built. (d) Capacity retention of different silicon nanostructures at rate of C/5. (e) Lithiation/delithiation capacity and CE of DWSiNTs cycled at 12 C with no significant capacity fading after 6000 cycles.

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improve the surface area but reduce the self-aggregation is needed to further enhance the energy-storage device performance. Porous materials have been widely used in various fields such as heterogeneous catalysis, adsorption, separation, gas storage, sensing, and so forth (Vu, Qian, & Stein, 2012). Electrical energy storage systems, including batteries and supercapacitors, can profit from porous structure. They have the advantages such as good access of the electrolyte to the electrode surface, large surface area facilitating charge transfer across the electrode–electrolyte interface, increased utilization of active material, and suppressed phase transformations/structure degradations during cycling. Thus, combining the advantages of both nanowires and porous structures can endow largely enhanced properties for energy storage application.

Porous ZnCo_2O_4 nanowires (Figure 16.7(a)) synthesized via a simple microemulsion-based method followed by an annealing approach exhibit a greatly increased surface area ($\sim 68.86 \text{ m}^2/\text{g}$) (Du et al., 2011). Applied as LIB anode, it showed superior capacity (1331.5 mAh/g) and only 10% loss after 20 cycles (Figure 16.7(b)). Jiang, Ma, and Li (2012) reported hierarchical porous NiCo_2O_4 nanowires through a facile polyethylene glycol-directed technique at room temperature followed by a suitable thermal treatment. Chen's group (Zhang, Cheng, Yang, and Chen, 2013) reported ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) porous nanorods obtained by firing LiCH_3COO , $\text{Ni}(\text{CH}_3\text{COO})_2$, and Mn_2O_3 . The resultant LNMO porous nanorods exhibited excellent long-term cyclability and high-rate capability, delivering a 20 C discharge capacity of 109 mAh/g and 5 C capacity retention of 99% up to 300 cycles. The results would shed light on developing metal oxide-derived electrode materials with porous nanowires and superior electrochemical performance.

Mesoporous V_2O_5 nanofibers with a specific surface area of $97 \text{ m}^2/\text{g}$ were synthesized via electrospinning followed by annealing treatment. The mesoporous nanofibers consisted of orthorhombic V_2O_5 with a small amount of residual carbon, and demonstrated a significantly enhanced Li storage capacity of 370 mAh/g and excellent cyclic stability (Yu, Chen, et al., 2011). Mesoporous VN nanowires (MVNNs) were successfully synthesized through hydrothermal synthesis and subsequent thermal nitridation under NH_3 atmosphere (Xiao et al., 2013). A versatile and effective method was present for fabricating thin, lightweight, and flexible freestanding MVNN/CNT hybrid electrodes, which exhibited excellent electrochemical performance. Wei et al. (2014) introduced a one-pot synthesis of hierarchical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ mesoporous nanowires (LVP/C-M-NWs) (Figure 16.7(c)). During hydrothermal process, the organic molecules located in the interstitial space of the aggregated composite assembled into mesochannels. Meanwhile the self-assembly of organic surfactants and the hydrolysis of LVP colloids resulted in the nanowire morphology. After *in situ* carbonizing of the surfactants along with the crystallization of LVP, the final mesoporous nanowire structure is obtained. As cathode for LIBs, the mesoporous composites exhibited greatly enhanced performance compared to the carbon-coated composites (Figure 16.7(d)).

Porous nanowire catalysts are becoming a hot spot in research because they are not only an excellent catalyst themselves but also provide continuous free oxygen diffusion channels to enhance catalytic and cycling properties in Li–air batteries. Mai's group (Zhao, Xu, et al., 2012) synthesized hierarchical mesoporous perovskite structure $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.91}$ (LSCO) nanowires (Figure 16.7(e)) as catalysts, which

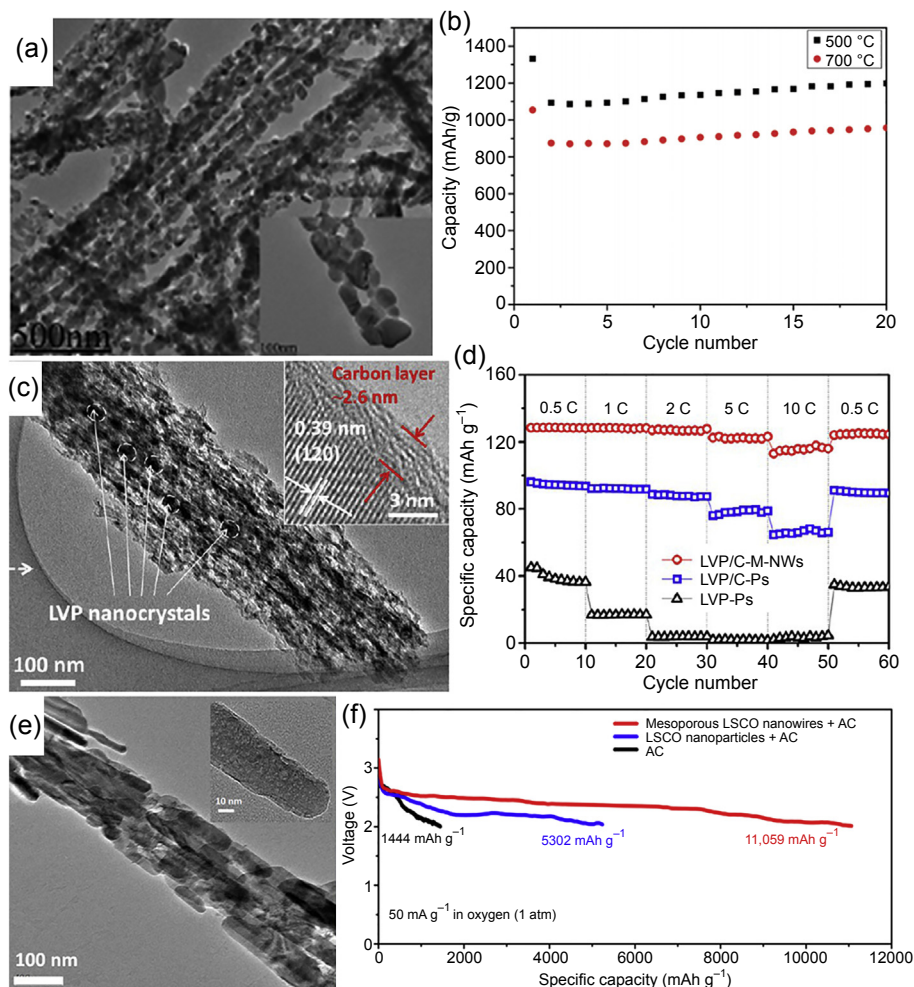


Figure 16.7 (a) TEM image of ZnCo_2O_4 porous nanowires. (b) Discharge capacity versus cycle number for the ZnCo_2O_4 nanowires electrodes. (Reprinted with permission from [Du et al. \(2011\)](#). Copyright 2011 American Chemical Society.) (c) TEM images of LVP/C-M-NWs. (d) Rate performance of the LVP/C-M-NWs. (Reprinted with permission from [Wei et al. \(2014\)](#). Copyright 2014 American Chemical Society.) (e) TEM images of the hierarchical mesoporous LSCO nanowires. (Inset shows porous LSCO nanorods from mesoporous nanowires.) (f) The discharge curve of Li-air batteries using hierarchical mesoporous LSCO nanowires and AC as the air electrode in oxygen.

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exhibited ultrahigh capacity over 11,000 mAh/g, with the improvement of one order of magnitude over LSCO nanoparticles (Figure 16.7(f)). LSCO nanorods were tightly attached to each other at the atomic level and formed the hierarchical nanowire. This structure could provide continuous oxygen diffusion channels, which greatly enhanced the electrocatalytic performance. Perovskite-based porous $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanotubes (PNT-LSM) were prepared by combining the electrospinning technique with a heating treatment (Xu et al., 2013). The synergistic effect of the high catalytic activity and the unique hollow channel structure of the perovskite-based porous $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanotubes electrocatalyst maximized the availability of the catalytic sites and facilitated the diffusion of electrons and reactants, which endowed the Li–air battery with a high specific capacity, superior rate capability, and good cycling stability (Zhou, Cheng, et al., 2011).

16.4.3 Hierarchical nanowires

Although fabricating coaxial nanowires is a facile and efficient way to realize enhanced performance, it still has some limitations, such as the smaller surface area and active sites. For this reason, branched or tree-like hierarchical nanowire structures have been demonstrated to get rid of the limitations (Cheng & Fan, 2012). Branched nanowires not only work well against the aggregation issue, but also represent unique, three-dimensional (3D) building blocks for the “bottom-up” paradigm of nanoscience and nanotechnology. These indicate the potential to design novel electronic and electrochemical energy storage nanomaterials and nanodevices. In electrochemical energy storage devices, branched nanowires as electrodes can provide more Li diffusion pathways, better cycling stability and capability due to the synergistic effect of the backbone and branch materials. Many branched nanowires were reported and better electrochemical performance was achieved (He et al., 2012; Kim, Nam, Lee, Choi, & Kim, 2011; Liu, Jiang, Bosman, et al., 2012; Liu, Jiang, Cheng, et al., 2011; Yang, Wang, et al., 2013; Zhou, Cheng, et al., 2011; Zhao, Lu, et al., 2012; Zhou, Yang, et al., 2011). Mai, Yang, et al. (2011) synthesized hierarchical $\text{MnMoO}_4/\text{CoMoO}_4$ nanowires with greatly enhanced performance. The heterostructures were successfully prepared on the backbone material by a convenient refluxing method under mild conditions. The crystal growth mechanism during the complicated nano-architecture process was “self-assembly” and “oriented attachment” (Figure 16.8a,b). The specific capacitance and energy density of asymmetric supercapacitors based on hierarchical $\text{MnMoO}_4/\text{CoMoO}_4$ heterostructured nanowires was significantly higher than that for pure 1D nanorods and simple mixed $\text{MnMoO}_4/\text{CoMoO}_4$ nanocomposite. Also, the hierarchical nanowire electrode shows good reversibility, with a cycling efficiency of 98% after 1000 cycles. Besides, the hierarchical $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$ nanowires had a significantly large active surface area to incorporate more Li ions, and this structure can prohibit the structure degradation during cycling, thus improving the cycling stability (Zhou, Cheng, et al., 2011).

Organic-inorganic branched nanowire composites were also investigated. Hierarchical $\text{MoS}_2/\text{Polyaniline}$ (PANI) nanowires were successfully synthesized via facile hydrothermal process (Yang, Wang, et al., 2013). In the synthesis process,

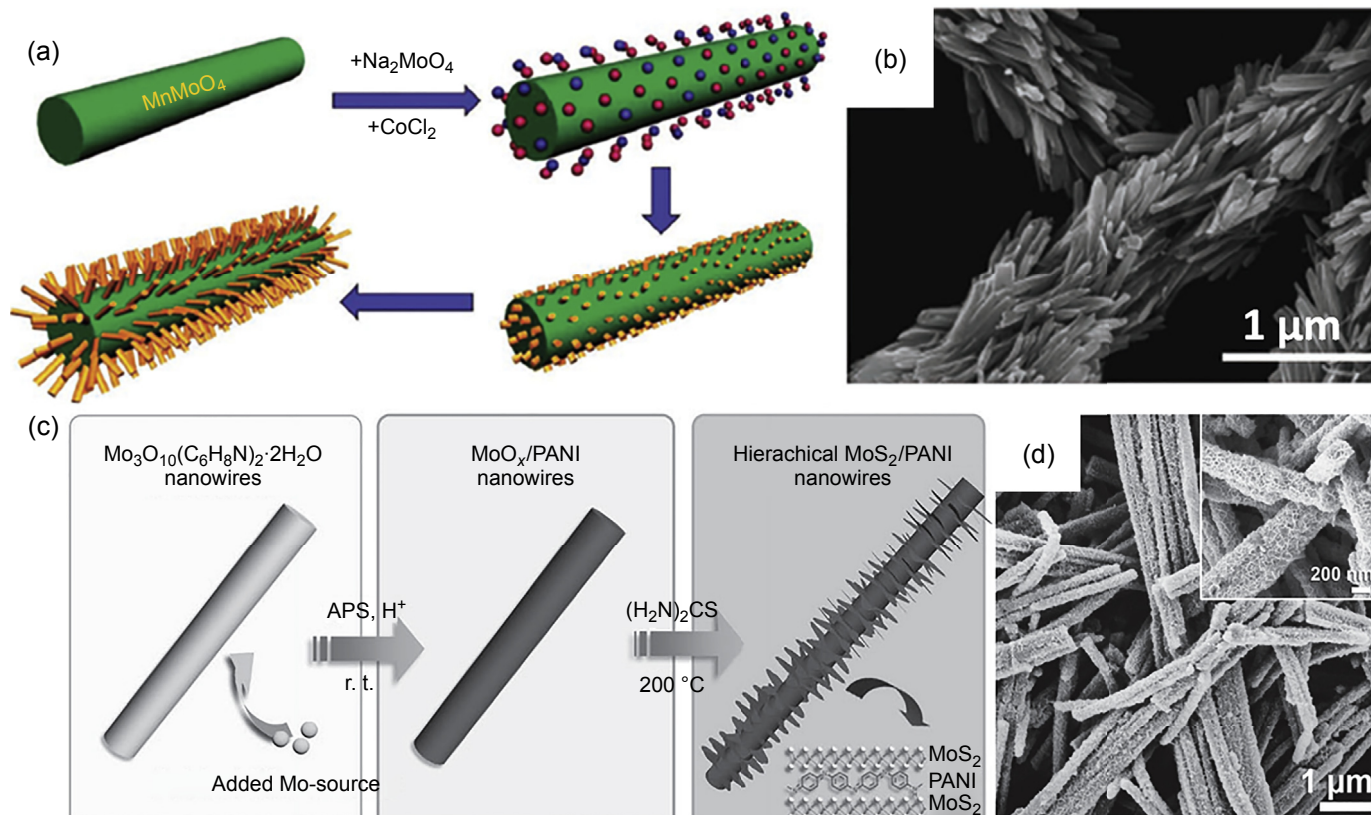


Figure 16.8 (a) The construction of hierarchical $\text{MnMoO}_4/\text{CoMoO}_4$ nanowires. (b) SEM images of hierarchical $\text{MnMoO}_4/\text{CoMoO}_4$ heterostructured nanowires. (Reprinted with permission from [Mai, Yang, et al. \(2011\)](#). Copyright 2011 Nature Publishing Group.) (c) Scheme for the fabrication of hierarchical MoS_2/PANI nanowires through facile polymerization and hydrothermal-treatment. (d) Typical SEM images of the as-obtained hierarchical MoS_2/PANI -III nanowires. Reprinted with permission from [Yang, Wang, et al. \(2013\)](#). Copyright 2013 John Wiley & Sons, Inc.

MoO_x/PANI nanowires were first synthesized after polymerization, and then converted to MoS₂/PANI via hydrothermal process with thiourea (Figure 16.8(c) and (d)). The as-obtained products evenly integrated MoS₂ ultrathin nanosheets with PANI into the primary 1D architecture, resulting in the novel hierarchical and polymer hybrid nanowires. By adding a varied amount of additional Mo-source, the contents of MoS₂ and PANI in nanowires were controlled. These unique MoS₂/PANI nanowires exhibited greatly improved Li storage ability owing to the hierarchical textures and the PANI hybrid structures. The charge capacity of 1063.9 mAh/g was obtained at 100 mA/g and retained 90.2% of the initial reversible capacity after 50 cycles. The branched nanowires are a more complicated form of exterior design. Combined with coaxial nanowires, both of them can improve the electrochemical performance, as they take advantage of the synergistic effect of the core materials and shell materials.

16.4.4 Nanowire arrays

Different from disordered nanowires, nanowires can vertically grow on substrates to form an aligned array, which offers an effective way to overcome the self-aggregation issue and the volume expansion caused mechanical degradation due to large volumetric strains (Figure 16.9) (Chan et al., 2008; Jiang et al., 2011). As each nanowire is fixed in a certain position and separated from one another, such architecture brings several advantages. First, the detached state of nanowires can greatly reduce self-aggregation, and free space between them could promote facile strain relaxation during battery operation. Second, nanowires are attached to the current collector for good adhesion and form continuous conducting pathways for electrons, which makes the binder-free and conducting additives-free. Third, ordered nanowire architectures, compared with nanowires with disordered form, have a larger specific surface area and lower average concentration of structural defects and grain boundaries, resulting in increased Li⁺ ions insertion/extraction rate and electrical transport.

Meduri et al. (2012) reported a chemical vapor deposition method to grow MoO_{3-x} nanowire arrays on metallic substrates with diameters of ~90 nm, and the nanowires show high capacity retention. Chen et al. (2013) developed a general method for facile kinetics-controlled growth of aligned arrays of mesocrystalline SnO₂ nanorods on arbitrary substrates by adjusting supersaturation in a unique ternary solvent system. Han et al. (2012) also reported a substrate-assisted hydrothermal method in synthesizing mound-lily-like aligned β-AgVO₃ nanowire clusters. Gravitation and F⁻ ions have been demonstrated to play important roles in the growth of β-AgVO₃ nanowires on substrates. The mound-lily-like β-AgVO₃ nanowire cathode had a high discharge capacity and excellent cycling performance, mainly due to the reduced self-aggregation. These arrays were grown directly on a conductive substrate, providing a direct current path to the electrode, which enhanced the rate capability. Further increasing the surface area and providing more volume expansion space, single-crystalline mesoporous Co₃O₄ nanowires were fabricated using a solution-based approach (Li, Tan, & Wu, 2008). An irreversible capacity loss was observed after the first discharge cycle, followed improved reversibility in subsequent charge–discharge cycles, resulting in a capacity of 700 mAh/g after 20 cycles. Additionally, 50% of the capacity was retained at

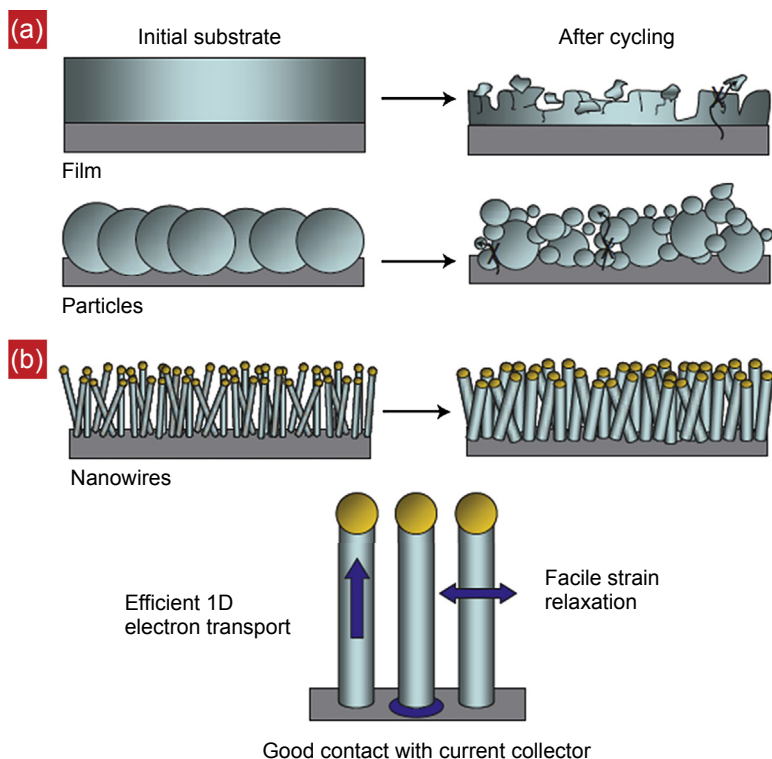


Figure 16.9 Schematic of morphological changes that occur in Si during electrochemical cycling. (a) The volume of silicon anodes changes by about 400% during cycling. As a result, Si films and particles tend to pulverize during cycling. Much of the material loses contact with the current collector, resulting in poor transport of electrons, as indicated by the arrow. (b) NWs grown directly on the current collector do not pulverize or break into smaller particles after cycling. Rather, facile strain relaxation in the NWs allows them to increase in diameter and length without breaking. This NW anode design has each NW connecting with the current collector, allowing for efficient 1D electron transport down the length of every NW. Reprinted with permission from [Chan et al. \(2008\)](#). Copyright 2011 Nature Publishing Group.

a discharge rate of 50 C, confirming the benefits of short ionic diffusion lengths in nanowire electrodes.

The high performance of a battery electrode relies largely on the design of nanoarchitectures. Fan's group ([Xia, Tu, Zhang, Chen, et al., 2012](#)) reported a fabrication of porous metal hydroxide nanosheets on a preformed nanowire array by a fast and well-controllable electrodeposition method. $\text{Co}(\text{OH})_2$ nanosheets were electrochemically deposited on the Co_3O_4 core nanowires to form core/shell arrays. Such oxide/hydroxide core/shell nanoarrays can be grown on different conductive substrates ([Figure 16.10](#)). After annealing the $\text{Co}_3\text{O}_4/\text{Co}(\text{OH})_2$ sample, the mesoporous homogeneous Co_3O_4 core/shell nanowire arrays were obtained and applied as anode material for LIBs. A high capacity of 1323 mAh/g at 0.5 C and excellent cycling stability

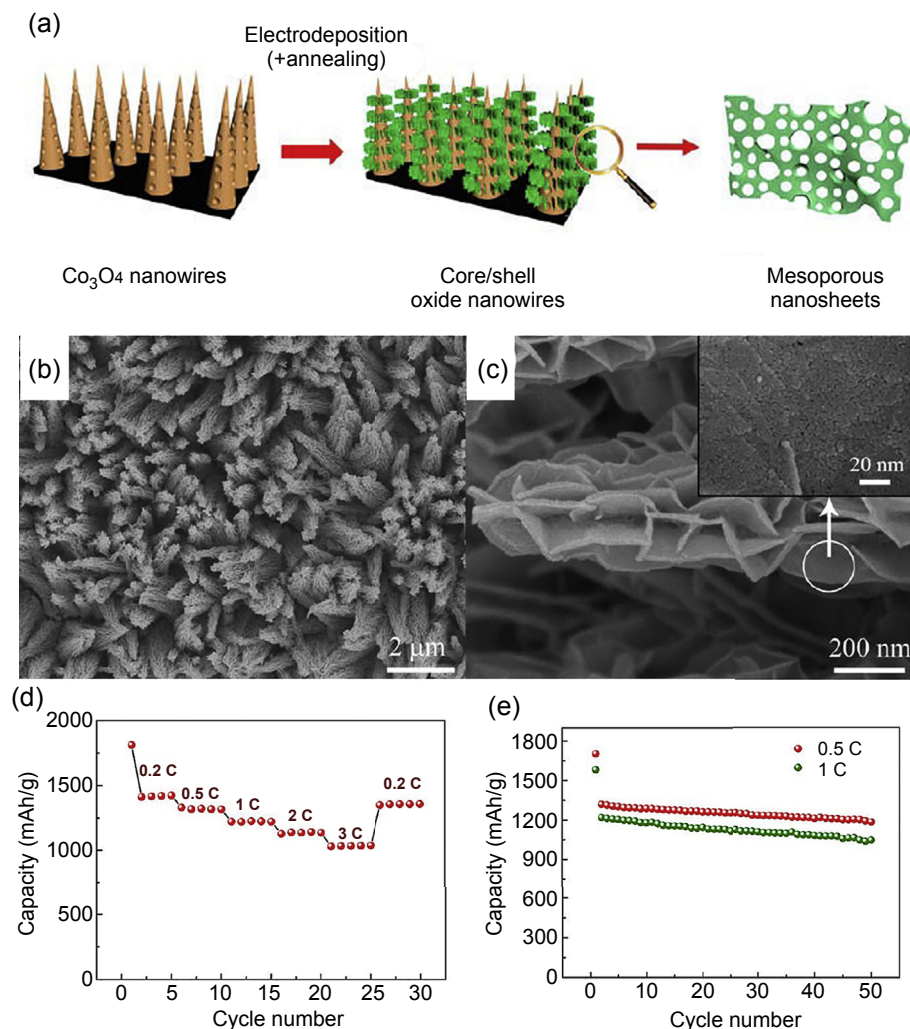


Figure 16.10 (a) Schematic of porous hydroxide nanosheets formed by electrodeposition on preformed nanowire arrays. The hydroxide sheets can be converted into oxides by thermal annealing. (b, c) SEM images of the Co_3O_4 core/shell nanowire arrays. Rate capability (d) and (e) cycling performance at different rate of mesoporous Co_3O_4 homogeneous core/shell nanowire arrays.

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were demonstrated (Figure 16.10(d) and (e)). Liu, Jiang, Cheng, et al. (2011) synthesized $\text{Co}_3\text{O}_4@\text{MnO}_2$ ultrathin nanosheet core/shell arrays, in which the MnO_2 nanosheets were grown on the Co_3O_4 backbone nanowire arrays. Both MnO_2 and Co_3O_4 components were electrochemical active compounds, while the Co_3O_4 nanowires provided direct electron transport pathway. The MnO_2 nanosheets were interconnected

with each other, forming a highly porous surface morphology, which offered high surface area and enabled the infiltration of the surface, resulting in excellent electrochemical performance. Besides those mentioned, many similar structures, such as NiO/MnO₂ hybrid tubular arrays (Liu, Jiang, Bosman, et al., 2012) and Co₃O₄/Mn(OH)₂ nanowire arrays (Xia, Tu, Zhang, Chen, et al., 2012) were also fabricated, demonstrating enhanced electrochemical performance by constructing the hybrid nanowire arrays.

16.5 Conclusions

Different from bulk materials, nanowire electrodes offer great improvement of energy storage devices due to its large electrode-electrolyte contact area, short ionic/electronic transport pathways and facile strain relaxation for volume change during cycling. A trend increasing in recent years is to utilize nanotechniques for *in situ* characterization of materials during device operation, which further explore the fundamental mechanism of energy storage, capacity fading and the direct relationship among electrical transport, structure, and electrochemistry of nanowire electrode materials. In the future, the combination of these techniques to probe multiple processes simultaneously will provide additional breakthroughs.

Another important development is to improve the design and fabrication of multifunctional nanosystems rather than simply focusing on the individual components, based on the improved understanding of the dynamics of the electrochemical storage processes. In addition, large-scale assembly of nanowires with high throughput and low cost will be critical for commercial adaptation of these technologies. Considering that nanowire electrodes possess novel structure and versatile properties, there still exists the tremendous possibility and potential of constructing high-performance, multifunctional, and hybrid electrochemical devices. It can be expected that the novel flexible, wearable, and transparent energy storage devices will be deeply developed by the utilization of nanowire structures. Moreover, together with the high-performance nanowire-based energy-storage devices, it will become an emerging and important technique to integrate energy storage devices with a range of novel functional electronic and mechanical micro/nano-devices. The evolution of nanowire electrode-based energy-storage devices will impact many fields and open up a whole new area in the future.

Acknowledgements

The author would like to acknowledge the financial support provided by the National Basic Research Program of China (2013CB934103, 2012CB933003), the National Natural Science Fund for Distinguished Young Scholars (51425204) the International Science & Technology Cooperation Program of China (2013DFA50840), National Natural Science Foundation of China (51072153, 51272197), the Hubei Province Natural Science Fund for Distinguished Young Scholars (2014CFA035) and the Fundamental Research Funds for the Central

Universities (2013-VII-028, 2013-ZD-7). I would like to thank Prof. C. M. Lieber of Harvard University, Prof. D. Y. Zhao of Fudan University, and Prof. J. Liu of Pacific Northwest National Laboratory for their stimulating discussion and kind help. The author thanks Q. L. Wei, X. C. Tian, Q. Y. An, and M. Y. Yan for their help.

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Semiconductor nanowires for biosensors

17

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17.1 Introduction

Sensitive detection of chemical and biological targets is central to many areas of fundamental life sciences, ranging from diagnosing disease to screening new drug molecules. The development of new sensor approaches that enable direct, sensitive, and rapid molecular analysis can significantly benefit human life. Many semiconducting nanomaterials, such as quantum dots (Wang, Yu, Xu, & Chen, 2009), carbon nanotubes (Liu, Tabakman, Welsher, & Dai, 2009), and nanowires (NWs) (Patolsky, Timko, Zheng, & Lieber, 2007) have been studied for the electrochemical sensing. Among them, NWs with their tunable morphology, structure, and electrical properties, combined with tailorable surface functionalization, provide a powerful approach to chemical/biomolecule sensing (Wang et al., 2013). As the diameters of the structures are typically in the range of 10 to 100 nm, which are comparable to many of the chemical and biomolecules (e.g., proteins and nucleic acids), NWs configured as field-effect transistors (FETs) are capable of providing a unique and powerful platform for chemical/biological recognition, which allows for conversion of molecular reactions into electrical signals. In addition, the capability of massive production and parallel fabrication of NW FET sensor devices allows for tens to hundreds of individually, electrically addressable NW devices to be defined within a single microfluidic sample delivery channel. By defining distinct receptors on the NW surface, this sensor platform provides an attractive opportunity of simultaneously detecting a wide range of chemical and biological molecules (Patolsky et al., 2007).

In this chapter, we first briefly introduce the fundamental principle of the NW FET sensors. Then, representative examples in which FET sensors are applied to detect chemical and biomolecule targets, including proteins, nucleic acids, viruses, and small molecules, are summarized. Furthermore, several methods for improving the sensitivity of semiconductor NW FET sensors, such as designing the branched NWs for enhanced capturing efficiency of molecular analytes, functioning in the FET sub-threshold regime, reducing the Debye screening length, increasing the analyte concentration by the electrokinetic effect, measuring the frequency distribution of the electrical signals, designing NW–nanopore sensors and double-gate NW sensors, the piezoelectric effect enhancement, and the detection in physiological fluids, are briefly illustrated. Finally, comments on the current challenges and future trends are provided.

17.2 Fundamental principle for FET sensors

FETs are among the fundamental building blocks of today's high-density integrated circuits. In a standard planar FET (Figure 17.1(a)), the semiconductor substrate (e.g., p-Si) is connected to the gate (G), the source (S), and the drain (D) electrodes. The source and drain regions, through which a current is injected and collected, respectively, have an opposite doping (e.g., n-type) to the substrate. The gate electrode is capacitively incorporated to the semiconductor channel by an insulating oxide layer. If no gate voltage is applied (the "off" state), the FET is equivalent to two p–n junctions connected back-to-back with almost no current flows. In the "on" state, when the gate bias exceeds a threshold voltage, carriers (e.g., holes for p-Si and electrons for n-Si) are induced at the semiconductor–oxide interface, and the potential barrier of the channel drops, resulting in a significant tunneling current flow. Therefore, the conductance of the semiconductor channel between the source and drain regions can be switched on and off by the potential at the gate electrode.

The use of planar FETs for ion-selective sensors was introduced several decades ago (Janata, 1994), while the nanoscale dimension and one-dimensional (1D)

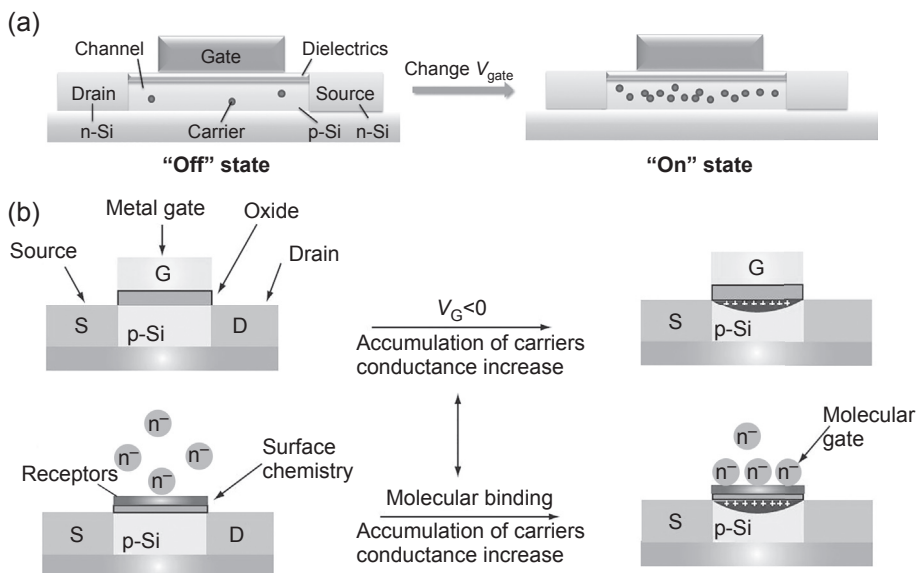


Figure 17.1 (a) A typical planar FET. The semiconductor substrate (e.g., p-Si) is connected to gate (G), source (S), and drain (D) electrodes, and can be switched between the "off" and "on" states by applying the gate voltage. (b) Schematic comparison between (top) a standard FET device and (bottom) a SiNW FET sensor. The NW surface is functionalized with a receptor layer to recognize target biomolecules in a solution, which are charged and provide a molecular gating effect on SiNWs.

Reproduced from Patolsky et al. (2006b), *Nanomedicine*, with permission from Future Medicine Ltd.

morphology of NWs further enhance their impact as chemical and biological sensors. Similar to planar FET, the conductance of an NW FET can be controlled by variations in the charge density or electric potential at the channel region, making FETs ideal candidates for chemical and biological sensing, as the electric field resulted from the binding of a charged molecule to the NW surface is analogous to applying a voltage via a gate electrode. In a p-type silicon NW (SiNW) functionalized with surface receptors that can specifically capture chemical/biomolecule targets, binding of molecules with negative charges (similar to applying a negative gate voltage) leads to accumulation of charge carriers (holes) and a corresponding increase in conductance (Figure 17.1(b)). However, binding of molecules with positive charges (similar to applying a positive gate voltage) will deplete holes and subsequently reduce the conductance. Hence, NW FETs enable the label-free, electrical readout as a unique sensing modality, which allows for the direct conversion of biological events, such as binding, enzymatic reaction, and electron transfer, into signals that can be electrically detected, thus providing a platform to analyze the biological samples in a facile means.

Semiconductor NWs composed of Si or other materials (e.g., ZnO, SnO₂, and In₂O₃) have been selected as candidates for the development of FET sensors. Among them, SiNWs can be prepared as single-crystal structures with diameters as small as 2 to 3 nm, and have been shown to exhibit performance characteristics comparable or even superior to the best achieved in the microelectronics industry. In addition, when integrated into device arrays and miniaturized systems, SiNW sensors can perform multiplexed screening of a variety of target biomolecules, with minimum sample consumption. Moreover, the development of SiNW sensors can benefit from the existing and mature silicon industry processing techniques, thus leading to excellent potential of interfacing with the top-down fabrication approaches (Wang et al., 2013).

SiNW FETs are transformed into nanosensors by surface functionalization of probe molecules that enable the specific recognition of chemical/biological molecule targets. The covalent binding is one of the most prevalent approaches to attach probe molecules on the SiNW surface, in which a native oxide (SiO₂) layer that naturally grows on SiNWs is utilized. A detailed surface functionalization process is described elsewhere (Patolsky, Zheng, & Lieber, 2006a). The simplest and earliest established example of this approach is hydrogen-ion concentration detection or pH sensing (Cui, Wei, Park, & Lieber, 2001). The SiO₂ layer at a p-SiNW surface is modified with 3-aminopropyl triethoxysilane (APTES), which yields amino group (–NH₂) termination on the NW surface (Figure 17.2(a)). The amino groups and silanol groups (Si–OH) on the oxide layer undergo protonation and deprotonation as the hydrogen ion concentration varies, thereby changing the surface charge and the NW conductance. A stepwise increase of the NW conductance with discrete, stable changes in response of pH from 2 to 9 is demonstrated (Figure 17.2(b)). Following this discovery work, a number of biological targets, including proteins, nucleic acids, viruses, and small molecules, have been developed by covalent attaching distinct surface receptors on NWs, with multiplexed and real-time electrical detection capability (Chen, Li, & Chen, 2011; Patolsky, Zheng, & Lieber, 2006b).

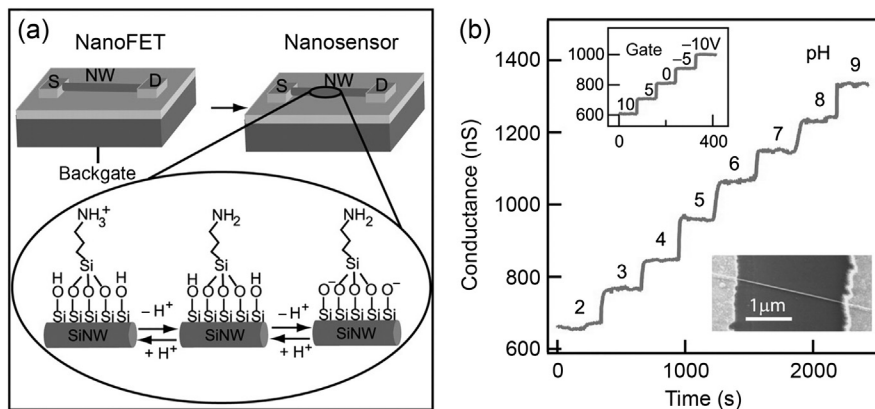


Figure 17.2 (a) Schematic of an amino-functionalized NW device and the protonation and deprotonation equilibria that change the surface charge state. (b) Changes in NW conductance as the pH of the solutions delivered to the sensor varies from 2 to 9.

Reproduced from Cui et al. (2001), *Science*, with permission from the American Association for the Advancement of Science.

17.3 Examples of semiconductor nanowire FET sensors

17.3.1 Protein detection

The sensitive detection of proteins, especially those known as disease markers, offers substantial potential in benefiting the disease diagnosis and treatment. In 2001, a pioneering work was demonstrated for protein sensing with p-SiNW FET devices (Cui et al., 2001). Specifically, SiNWs functionalized with biotin receptors are used to selectively detect streptavidin with concentrations down to 10 pM, substantially lower than other methods, such as stochastic sensing (Movileanu, Howorka, Braha, & Bayley, 2000). However, the irreversible strong binding affinity between biotin and streptavidin precludes the real-time monitoring of protein concentrations. Thus, several reversible surface modifications are further explored, such as biotin-monovalent antibody binding and the calmodulin (CaM)–Ca²⁺ interaction, to achieve consecutive quantitative protein analysis (Cui et al., 2001). Lin et al. (2010) used CaM-modified SiNWs to detect Ca²⁺ and CaM-binding proteins through the association/dissociation interaction between glutathione and glutathione S-transferase. Upon addition of the positively charged cardiac troponin I (TnI), the conductance of p-SiNW FET decreases significantly. The successful detection of cardiac biomarkers (Chua, Chee, Agarwal, Wong, & Zhang, 2009), SARS virus nucleocapsid proteins (Ishikawa, Chang, et al., 2009), and bovine serum albumin (Tian, Regonda, Gao, Liu, & Hu, 2011) reported in the literature further tests the efficacy of NW FETs as protein sensors.

In genomics and proteomics research, simultaneous detection of multiple proteins is especially important in diagnosis of complex diseases (e.g., cancers). Moreover, the availability of different biomarkers matched with different stages of diseases

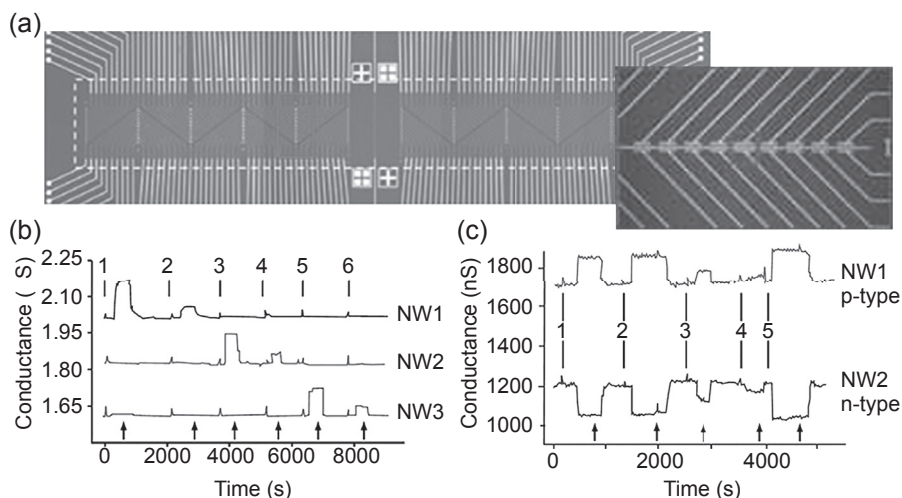


Figure 17.3 (a) Optical image of a portion of a nanowire array, where the inset shows one row of individually addressable elements. (b) Time-dependent conductance of three p-type SiNW FET sensors (NW1, NW2, NW3) functionalized with monoclonal antibodies, for detection of PSA, CEA and mucin-1 solutions sequentially delivered onto the sensor array. (c) Complementary sensing of PSA using p-type (NW1) and n-type (NW2) SiNW FET sensors in a same array.

Reproduced from [Zheng, Patolsky, Cui, Wang, and Lieber \(2005\)](#), *Nature Biotechnology*, with permission from Nature Publishing Group.

allows for early detection and robust diagnosis. The previous work on SiNW FET devices ([Cui et al., 2001](#)), although powerful in detecting binding/unbinding of proteins, lacks the capability of selective multiplexed sensing. To address this issue, integrated NW sensor arrays were developed in which ~ 100 individually, electrically addressable NW FETs were functionalized with several different receptors ([Figure 17.3\(a\)](#)) ([Zheng et al., 2005](#)). Specifically, three SiNW FET devices functionalized with monoclonal antibodies are demonstrated against three biomarkers—prostate-specific antigen (PSA), carcinoembryonic antigen (CEA), and mucin-1 ([Figure 17.3\(b\)](#)). Upon the addition of buffer solutions containing different concentrations of biomarkers, changes of electrical conductance of the corresponding NW FETs have been recorded at up to femtomolar sensitivity. Compared to other detection methods, such as the enzyme-linked immunosorbent assay (ELISA), the incorporation of different types of addressable SiNWs, such as p-type and n-type SiNWs in a same device, allows for simultaneous, complementary signal readout from the same biomarker solutions ([Figure 17.3\(c\)](#)). For instance, the linkage of negatively charged biomarkers (such as PSA, as its isoelectric point is lower than the pH of the buffer used) on the NW sensor surfaces leads to an increase in conductance for p-SiNW and a decrease for the n-SiNW conductance in the same sensor chip. These complementary, opposite electric signals can be used to distinguish false signals and enable real-time, highly sensitive detection of multiplexed biomolecule targets. Contemporaneously, Li and

coworkers reported the complementary sensing of PSA using n-type In_2O_3 NWs and p-type carbon nanotubes (Li et al., 2005). The enhanced electrical conductance for the NW sensors and the suppressed electrical signal for the carbon nanotube sensors upon the PSA addition are demonstrated with concentrations down to 5 ng/mL sensitivity at physiological buffer concentrations.

Later, an anisotropic wet-etch fabrication method was demonstrated to overcome the limitations of NW device fabrication and generate nondegraded sensors (Stern, Klemic, et al., 2007). Tetramethylammonium hydroxide (TMAH), with a slow Si (111) etching rate, is used to produce NWs with dominant Si (111) facets, that is, the preferred plane for surface modifications. This method is compatible with integrated circuit (IC) technology. The sensitivity of the obtained SiNW devices are demonstrated to be sub-100 fM for biotin–streptavidin interaction, mouse immunoglobulin G (IgG), and mouse immunoglobulin A (IgA) detection, as well as real-time live cell monitoring.

17.3.2 Nucleic acid detection

In addition to the protein binding/unbinding activities, the real-time detection of nucleic acids (e.g., DNAs and RNAs) has been successfully carried out by Si and GaN NW FET devices (Ganguly et al., 2009; Hahm & Lieber, 2004; Li et al., 2004). The surface functionalization methods and detection schemes are similar to the aforementioned protein sensing, in which the nucleic acid concentrations are translated into changes in device conductance. Furthermore, multisegment CdTe–Au–CdTe NWs modified with thiol-terminated DNA probes can also function as biomolecule sensors (Wang & Ozkan, 2008). The Au segment is applied as the binding site of single-strand DNA fragments due to its active surface functionalization capability, while the CdTe segments at both ends serve to modulate the Fermi level of the heterojunction device upon hybridization of the target DNAs to the Au segment. Compared to a homogeneous semiconducting NW sensor, the multisegment structure possesses an advantage in selective binding of probe molecules.

The major difference between nucleic acid and protein detections exists in the fact that the high density of negative charges on phosphate backbones of nucleic acids requires high ionic strength buffers to screen the repulsion between DNA or RNA strands. The high ionic strength, on the other hand, leads to a short Debye screening length (see Section 17.4.3). Thus, peptide nucleic acid (PNA), an artificially synthesized polymer similar to DNA, which exhibits excellent binding affinity with DNA, has been demonstrated to be an excellent surface-modification ligand (Hahm & Lieber, 2004). In contrast to DNA, PNA does not have an anionic phosphate backbone, and is therefore uncharged at neutral pH values, so that the binding of PNA/DNA or PNA/RNA can take place in low ionic strength buffers. The hybridization of negatively charged oligonucleotides on NW surfaces leads to accumulation of charge carriers in the device, resulting in a corresponding time-dependent conductance change. This process can effectively detect target DNA with concentrations as low as 10 fM. Notably, the detection can distinguish the fully complementary (wild type) versus single-base mismatched (mutant) DNA targets. Furthermore, SiNWs functionalized

with PNA molecules have also been used to illustrate the sensitivity dependence on the distance from the hybridization site to the NW surface (Zhang, Zhang, et al., 2008). The field effect becomes much weaker if the charge molecules are farther apart from the surface of SiNW sensors.

Besides the covalent binding scheme, the electrostatic adsorption has also been utilized for surface functionalization of SiNW devices, which involves electrostatic attraction between ionic solutes and oppositely charged receptors. It has been reported that the electrostatic adsorption of primary DNA onto an amine-terminated SiNW surface, which allows for circumvention of the Debye screening, is useful for sensitive DNA detection (Bunimovich et al., 2006). The native oxide layer on SiNW devices, although bringing convenience for subsequent functionalization, may limit sensor performance due to the formation of interfacial electronic states. In addition, the silicon oxide layer, which acts as a dielectric, may screen the sensor from chemical detection. In contrast, SiNWs reported in this work are directly coupled with an alkyl layer, and thus exhibit much better sensitivity and dynamic range, compared to NWs covered by an oxide layer.

The detection of other nucleic acid targets using PNA-modified SiNWs has also been demonstrated. For instance, microRNAs (miRNAs) are a large class of short, noncoding RNA molecules that regulate animal and plant genomes, and can serve as biomarkers for cancer diagnosis (Wang et al., 2013). PNA-functionalized SiNW devices have been applied to the detection of ultralow concentrations of miRNAs down to a remarkable sensitivity of 1 fM (Zhang, Chua, Chee, Agarwal, & Wong, 2009), about one magnitude higher than the previous report for DNA detection (Zhang, Chua, et al., 2008). This phenomenon can be attributed to the higher thermal stability and melting temperature of the PNA–RNA complex than that of the PNA–DNA complex. The technique enables identification of fully complementary versus one-base mismatched miRNA sequences, as well as detection of miRNA in total RNA extracted from HeLa cells.

17.3.3 Virus detection

Viruses are the major cause of infectious diseases, which remain the world's leading cause of death. Diagnostics and treatment of these diseases, therefore, requires rapid and accurate identification of viruses at ultralow concentrations (Zhang & Ning, 2012). One of the earliest demonstrations of SiNW FETs as virus sensors involves the detection of influenza A virus, the cause of outbreaks of respiratory infection ranging from self-limited to severe illness. By recording the corresponding electrical conductance changes upon binding/unbinding of virus particles on monoclonal antibody-modified SiNWs, the selective detection of influenza A at the single-particle level has been demonstrated (Patolsky et al., 2004). The real-time, electrical detection of virus also provides direct information about binding kinetics crucial to understanding of virus–receptor interactions (Figure 17.4). Also in this work, simultaneous detection of two viruses using independent SiNW biosensor arrays functionalized with distinct antibodies has been carried out, in which influenza A and adenovirus are detected in parallel. In a more recent report, it further demonstrates

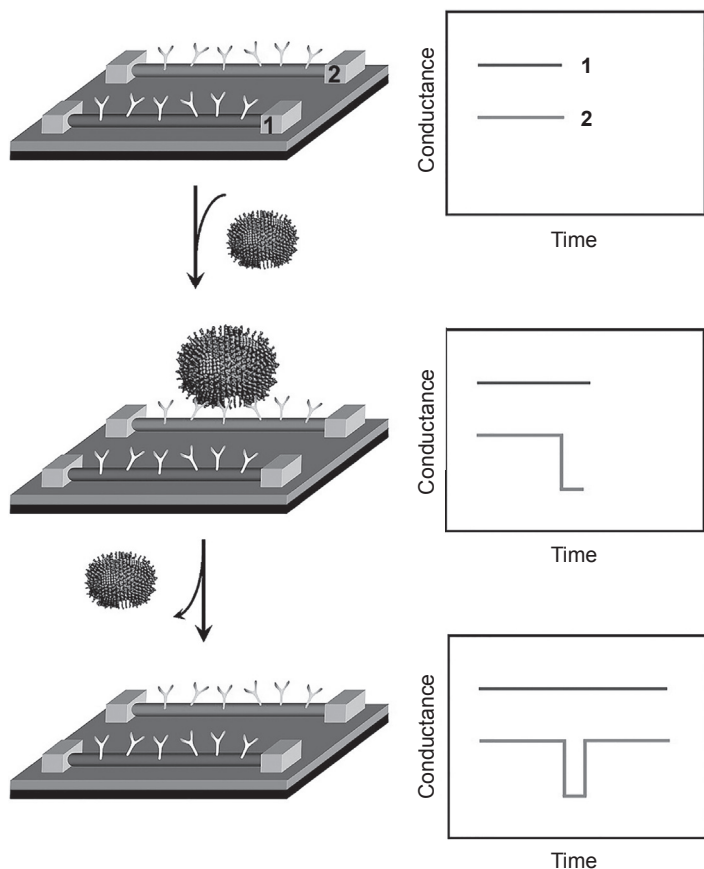


Figure 17.4 Schematic of a single virus binding and unbinding to the surface of a Si nanowire device modified with antibody receptors and the corresponding time-dependent change in conductance.

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the selective detection of influenza A viruses down to 29 viral particles per microliter clinical exhalates breath condensate samples, within minutes using SiNW FET sensors (Shen et al., 2012).

Another example of virus detection is the diagnosis of Dengue, a commonly prevalent arthropod-borne viral infection (Zhang et al., 2010). In this work, a specific fragment with 69 base pairs derived from Dengue serotype 2 virus genome sequences is selected as the target DNA and amplified by the reverse transcription polymerase chain reaction (RT-PCR). The hybridization of the target DNA and the PNA-functionalized SiNW FET sensors increases the device resistance, leading to a sensitivity limit down to 10 fM.

17.3.4 Small molecule detection

Detection of small molecules that bind specifically to proteins is of vital importance to drug discovery and screening. One example of small molecule detection involves the identification of adenosine triphosphate (ATP) binding, and the small molecule inhibition of ATP binding to the tyrosine kinase, Abl, which are proteins that mediate signal transduction in mammalian cells. Gleevec, which competitively inhibits ATP binding to Abl, has been used to monitor binding/unbinding behaviors of ATP. The Gleevec concentration at fixed ATP concentration yields a conductance decrease, which is consistent with reversible competitive inhibition of an agonist (ATP) with an antagonist (Gleevec) (Wang, Chen, Lin, Fang, & Lieber, 2005). Later, a highly ordered flexible SiNW film, fabricated by a scalable and parallel dry transfer process, has been applied to detect NO₂ with parts-per-billion (ppb) sensitivity (Mcalpine, Ahmad, Wang, & Heath, 2007). Other small molecules, such as ammonia (NH₃), acetic acid (AcOH) (Mcalpine et al., 2008), and 2,4,6-trinitrotoluene (TNT) (Engel et al., 2010), have also been successfully detected by surface-functionalized SiNW FET sensors.

Despite numerous approaches developed for achieving highly sensitive detection of polar molecules, the detection of nonpolar volatile organic compounds (VOCs) still remains challenging, due to the weak adsorption of nonpolar VOCs on the surface of NWs and the lack of suitable nonpolar organic functionalities that can be attached to the SiNWs. To address this issue, silane monolayer with a low fraction of Si—O—Si bonds between the adjacent molecules has been used to modify the SiNW FETs to enhance their sensitivity toward nonpolar VOCs (Paska, Stelzner, Christiansen, & Haick, 2011).

17.4 Methods for enhancing the sensitivity of semiconductor nanowire sensors

17.4.1 Three-dimensional (branched) nanowires for enhanced analyte capturing efficiency

Three-dimensional (3D) or branched NWs, in which secondary NW branches are grown in a radial direction from a primary NW backbone, provide the capability of achieving 3D connectivity. The ability to prepare rationally designed branched NWs, with well-controlled variations in the composition of the backbone and the NW branches, may enable realization of complex electronic and photonic nanodevices via encoding functionality synthetically at well-defined branch junctions. For instance, branched NW heterostructures, where SiNW backbone and Au branches serve as the semiconductor channel and the gate electrodes, respectively, have been demonstrated as FET biosensors (Figure 17.5(a)) (Jiang et al., 2011). The Au branches act as the receptor-functionalized “antennas” for the biomolecule analyte, and provide the potential to achieve enhanced capturing efficiency and sensitivity through the 3D connectivity and interconnection.

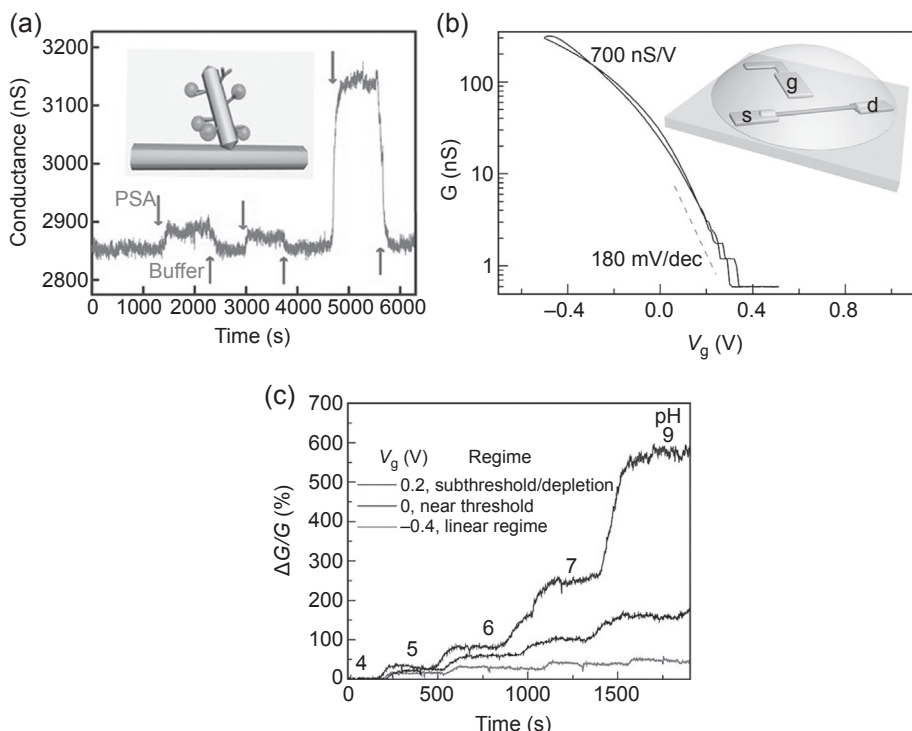


Figure 17.5 (a) Conductance versus time curve recorded on a p-Si/Au branched NW sensor with alternate delivery of PSA (4 ng/mL, 80 pg/mL, 200 ng/mL) and pure buffer solutions. The top and bottom arrows mark the delivery of protein and buffer solutions into the sensing channel. Inset: Schematic of Si/Au branched NW sensor. (Reproduced from Jiang et al. (2011), *Proceedings of the National Academy of Sciences of the United States of America*, with permission from the National Academy of Sciences of the United States of America.) (b) Conductance G versus electrolyte gate voltage V_g of a p-type SiNW FET. The inset shows the schematic of electrolyte gating. This device has a trans-conductance of ~ 700 nS/V in the linear regime and subthreshold slope $S \sim 180$ mV/decade in the subthreshold regime, with a threshold voltage $V_T \sim 0$ V. (c) Real-time pH sensing data as the percentage change, $\Delta G/G$, with the conductance value at pH = 4 as reference point. In the subthreshold regime ($V_g = 0.2$ V), the device shows much larger percentage change in conductance as solution pH changes. (Reproduced from Gao, Zheng, and Lieber (2010), *Nano Letters*, with permission from the American Chemical Society.)

17.4.2 Detection in subthreshold regime

The fundamental factors of NW FET devices can have a substantial effect on their sensitivity. It has been demonstrated that the sensitivity of SiNW FET sensors can be exponentially enhanced in the FET conductance subthreshold regime, in which the current varies exponentially with the gate voltage (Gao et al., 2010). Compared to the “normal” linear region (where the current is almost linearly dependent on the

gate voltage), the gating effect of biomolecules bound on the NW surface is significantly enhanced, due to the reduced screening of charge carriers inside the SiNW conduction channels (Figure 17.5(b)). In previous literature using SiNW FET sensors, the conductance change (ΔG) or the resistance change (ΔR) of the sensor devices is predominantly recorded to quantify the concentration of the target molecules. However, these absolute signal changes, such as ΔG , cannot reflect the intrinsic sensitivity due to their dependence on specific parameters of the NW devices, such as diameter and mobility. In this work, a dimensionless parameter, $\Delta G/G$, is used to characterize the device sensitivity. This principle is exemplified in both pH and protein sensing experiments, where the operational mode of the NW FET biosensors is tuned by the electrolyte gating (Figure 17.5(c)). This work shows that optimization of the NW FET structure and operating conditions can provide significant enhancement and fundamental understanding for the sensitivity limits of NW FET sensors.

17.4.3 Reduce the Debye screening effect

Conventional chemical FETs sense the concentration of the target species by their intrinsic charge. The charges of solution-based molecules, however, can be screened by dissolved counter ions in the solution. For example, the FET sensitivity of the negative-charged streptavidin molecules, which are surrounded by positively charged ions due to electrostatic force, is therefore reduced. The Debye length, or the Debye radius, refers to the measure of a charge carrier's net electrostatic effect in solution, and determines how far those electrostatic effects persist. Charges outside of the Debye length are electrically screened. In an electrolyte solution environment of a typical NW FET sensor, the high ionic strength subsequently leads to a short Debye length, which is inversely proportional to the square root of the ionic strength of a sensing buffer. For instance, the Debye length of $1 \times \text{PBS}$ (~ 0.7 nm, approximately the length of several base pairs) screens most of the protein's charges. In order to reduce the charge screening from the electrolyte solution, the Debye length is increased by using dilute buffer solutions with low ion concentrations, without affecting the oligonucleotide hybridization efficiency (Ishikawa, Curreli, et al., 2009; Stern, Wagner, et al., 2007).

17.4.4 Electrokinetic enhancement

Preconcentration by the electrokinetic manipulation of particles, with numerous advantages such as shorter detection time, increased concentrations, and flexible electrode design and fabrication, offers an alternative approach for high-sensitivity protein detection (Gong, 2010). In a nonuniform AC electric field, the dielectrophoresis force causes the polarized particles to move toward one particular direction, depending on the particle polarizability compared with the suspending medium, thus leading to the formation of concentration enhancement and depletion regions in the microfluidic flow channel. Compared to the detection limit without AC excitation, NW sensors modified with monoclonal antibody for PSA in a diverging AC field exhibit nearly a $\sim 10^4$ fold increase in sensitivity.

17.4.5 Frequency domain measurement

In addition to the conventional electrical measurement in real time, fluctuations in the NW FET electric signal at equilibrium can convey additional information about the dynamics of the biomolecule–NW hybrid system through a coupling to carrier transport in the device, such as intrinsic device noise due to mobility and carrier fluctuations and thermal fluctuations, known as the noise spectra (Figure 17.6(a)). In one study, the authors use the noise spectra in frequency domain to analyze contributions from different noise sources (Zheng et al., 2010). Specifically, the frequency domain spectrum of a two-level fluctuator system has the form of a Lorentzian function similar to that of an RC circuit (Figure 17.6(b) and (c)). The $1/f$ noise is well known in conventional metal-oxide semiconductor FETs (MOSFETs), arising from capture and emission of electrons from trap states. If the Lorentzian function associated with biomolecule hybridization on SiNW FET has a more significant contribution than other noise sources, it leads to a Lorentzian peak in addition to the $1/f$ spectrum background. As a result, both the frequency and conventional time domain measurements carried out on the same device show more than a 10-fold increase in sensitivity in the frequency domain data. Furthermore, the frequency domain noise spectra of SiNW FETs provide a means to study the NW–protein–solution interface, such as the molecular-binding kinetics and the thermal fluctuation of the molecular layer on NW sensor surface.

17.4.6 Nanowire–nanopore sensors

The integrated NW–nanopore FET sensor has the potential of performing single-molecule DNA sequencing at low cost and with high throughput. Different from conventional nanopore DNA sequencing in which the ionic current is recorded from individual nanopores, the NW–nanopore sensors allow for direct sequencing of DNA with a bandwidth consistent with fast translocation rates. The nanopore through

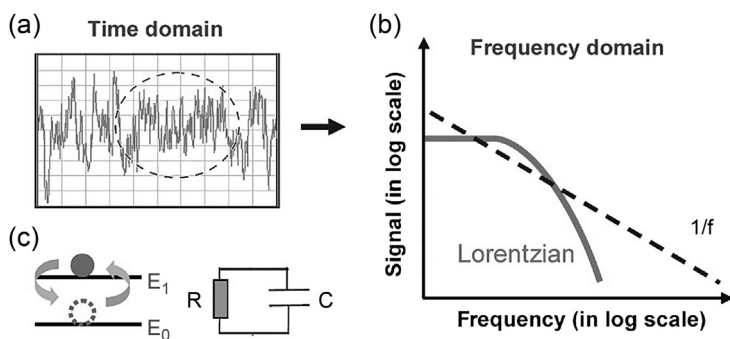


Figure 17.6 (a) Schematic of electrical noise in a time-domain measurement. (b) Schematic of Lorentzian and $1/f$ functions in the frequency domain. (c) Models of a two-level system (left) and a RC circuit (right).

Reproduced from Zheng, Gao, and Lieber (2010), *Nano Letters*, with permission from the American Chemical Society.

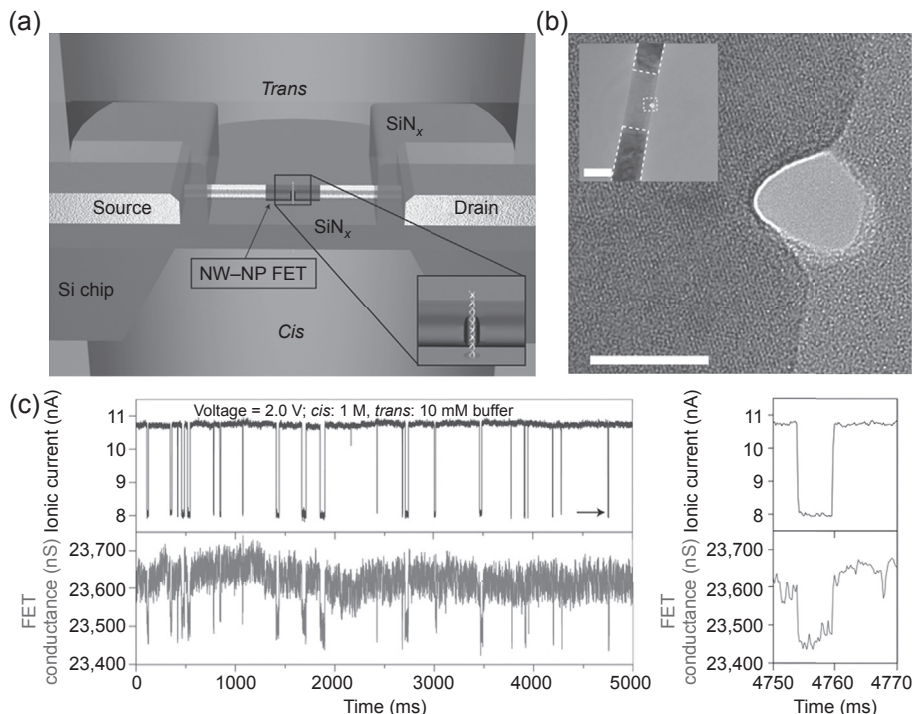


Figure 17.7 (a) Schematic of an SiNW–nanopore FET sensor. (b) TEM image of an SiNW–nanopore FET sensor. (c) Simultaneous recording of SiNW–nanopore FET conductance and the ionic current for detection of DNA translocation through the nanopore. Reproduced from [Xie, Xiong, Fang, Qing, and Lieber \(2012\)](#), *Nature Nanotechnology*, with permission from Nature Publishing Group.

the edge of the SiNW and the underlying silicon nitride membrane is created by focusing an electron beam via transmission electron microscopy ([Figure 17.7\(a\)](#)). Single-channel DNA translocation measurements are carried out with two polydimethylsiloxane (PDMS) solution chambers as reservoirs above and below the silicon nitride membrane, respectively. When the two chambers are filled with solutions of different ionic strength, well-defined FET conductance signals associated with DNA translocation can be recorded, as an ionic strength gradient is imposed across the nanopores ([Figure 17.7\(b\) and \(c\)](#)). The signal produced by the SiNW FET is 10 to 60 times higher than that of the ionic current change. This work provides an important basis for a new class of nanopore sequencing devices with the capability for fast direct sequencing and large-scale integration ([Xie et al., 2012](#)).

17.4.7 Double-gate nanowire sensors

In order to achieve high sensitivity of NW FET sensors, extensive efforts have been focused on advanced lithographic tools and size-reduction techniques.

A double-gate NW FET biosensor, with two separated gates, G1 (primary) and G2 (secondary), straddling both sidewalls of the SiNW, has been used to enhance the device sensitivity (Ahn et al., 2010). It has been proved that by applying the same voltage to G1 and G2, the threshold voltage (V_T) in the double gate mode is very sensitive to a small change of V_{G2} (the G2 voltage). Therefore, the sensing window can be significantly broadened compared to the case of a conventional single-gate FET sensor, especially in the subthreshold regime as described in Section 17.4.2.

17.4.8 Piezoelectric effect enhancement

For wurtzite and zinc-blende semiconductors, such as ZnO NWs, the compressive strain-induced polarization inside the materials can be used to tune the transport property, which is known as the piezotronic effect. In a recent report, the current of ZnO NW FET sensor increases substantially, and the shape of I – V curves changes from an “Ohmic type” to a “Schottky type” when the applied strain increases from 0% to 0.82%. That is because, by applying a strain, a piezopotential can be produced in ZnO NWs, which effectively tunes the Schottky barrier height, thus increasing the sensor resolution by tens of times and improving the detection limit and sensitivity substantially (Yu, Pan, & Wang, 2013).

17.4.9 Detection of biomolecules in physiological fluids

Rapid and accurate molecular analysis in physiological fluids (i.e., blood or serum) is essential for disease diagnosis and management. NW FET sensors, although powerful in ultrasensitive, real-time, multiplexed detection of multiple biomolecular species, exhibit some fundamental limitations regarding molecular sensing in complex physiological solutions. The reasons stem not only from nonspecific binding in the electrical measurements, but more importantly, from the high ionic strength in blood/serum samples that can cause severe Debye screening effect (Makowski & Ivanisevic, 2011).

To overcome the limitation of Debye length, researchers have developed methods to detect blood/serum samples in a controlled manner. One immediate method to reduce the ion concentration is to dilute the blood sample with a buffer solution (Kim, Lee, Yang, Jo, & Hahn, 2009). However, the diluting method has an impact on ligand–protein and protein–protein interactions (Lloret et al., 2013) and also reduces the analyte concentration, which would raise the requirement for the device sensitivity instead. The second approach is to desalt the serum samples before the multiplex detection of biomarkers (Zheng et al., 2005). However, it might lead to the loss of target proteins during the desalting step. The third method involves the introduction of a microfluidic purification chip (MPC) system to pre-isolate the target molecules and release them into a pure buffer suitable for sensing, followed by the analysis using SiNW FET arrays (Stern et al., 2010). The two-stage approach captures the targets from a complex environment such as a whole blood, and reduces its minimum required sample consumption by effectively preconcentrating the biomarkers. The fourth method is to adopt a steady-state measurement instead of a real-time recording. Initially, the first resistance of the SiNW is measured in a low ionic strength

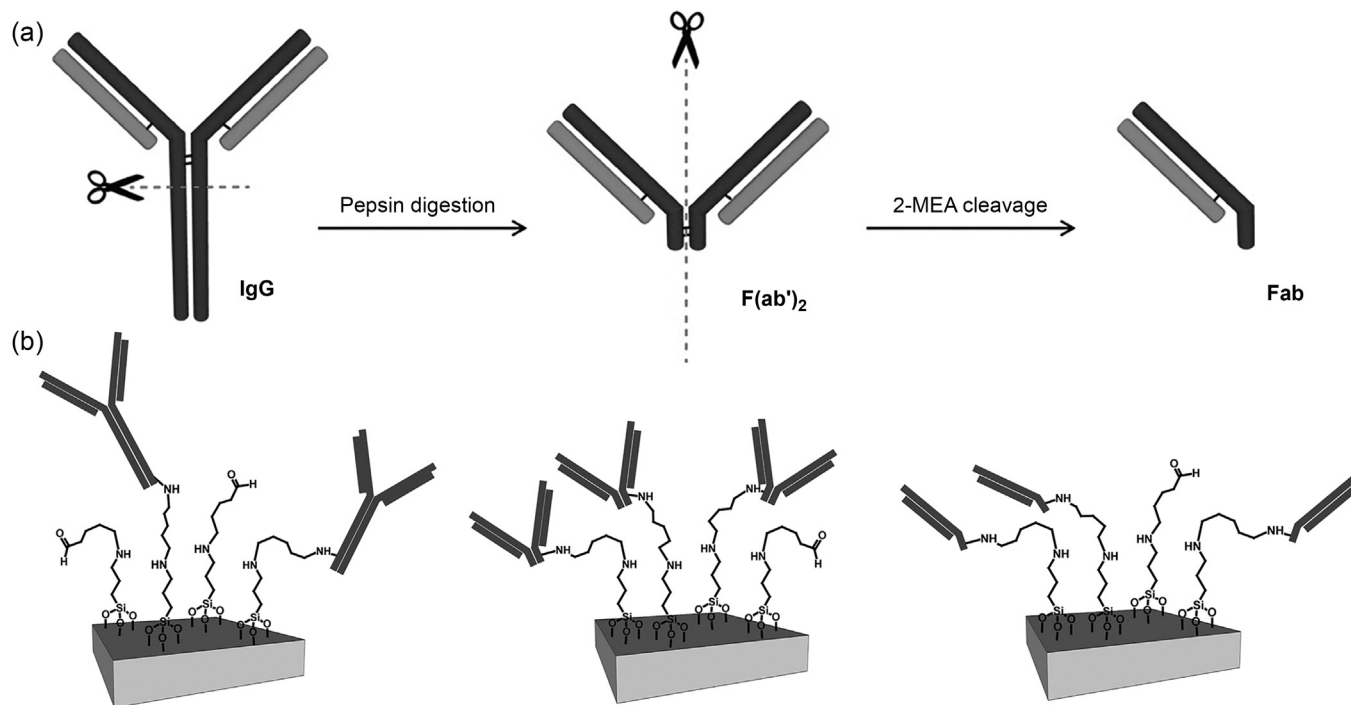


Figure 17.8 (a) Schematic for the generation of $F(ab')_2$ /Fab fragments from a whole IgG molecule. The enzyme pepsin degrades the heavy chains below the interchain disulfide bridges, leaving two Fab portions still connected via the hinge region [$F(ab')_2$]. Next, 2-mercaptoethylamine·HCl (2-MEA) is further used for selectively cleaving the hinge-region disulfide bonds between the heavy chains of the $F(ab')_2$ fragments and leaving two Fab molecules. (b) Schematic for the immobilization of a full IgG, $F(ab')_2$ and Fab antibody fragments that contain free amine groups onto the SiO₂ surface as receptor layers.

Reproduced from [Elnathan et al. \(2012\)](#), *Nano Letters*, with permission from the American Chemical Society.

buffer solution after antibody functionalization. Then, the SiNW sensor is incubated with undiluted serum and subsequently washed to remove unbound proteins, followed by the measurement of the second resistance value in the buffer solution (Zhang et al., 2012). The concentration of the target molecules can be calculated according to the resistance change before and after antibody–antigen interaction. This method is independent of the ionic strength of the sample solution, thus circumventing the Debye screening in physiological fluids. The fifth method is to use size-reduced antibody fragments, which allow for the biorecognition event to occur in closer proximity to the NW surface, falling within the Debye length (Elnathan et al., 2012). In this work, only the antigen-binding part of the antibody is used, instead of the whole antibody molecules (immunoglobulins, IgGs) (Figure 17.8(a)). In this approach, the sizes of antibody molecules are reduced through common molecular bioengineering methods (Figure 17.8(b)), and thus both the signal transduction efficiency and the detection capability are improved.

17.5 Conclusion

In this chapter, we have illustrated how the NW-based FET sensors modified with specific surface receptors represent a powerful chemical/biomolecule detection platform. The examples described here summarize several unique capabilities for direct, label-free, real-time, ultrasensitive and highly selective multiplexed detection of proteins, nucleic acids, viruses, and small molecules. The capability to enhance the device sensitivity of NW sensors, both in a structural and schematic point of view, is important for, and drives, the scientific breakthroughs that can enable revolutionary advances in chemical/biological detection technologies. The rational design of these sensing mechanisms has enabled, and will continue to inspire, exploring the limits of NW FET sensors, investigating a broad range of scientific problems, discovering new concepts, and ultimately driving technologies of the future.

17.6 Future trends

Between 2000 and 2010, remarkable research progress has been made on the design and implementation of semiconductor NW sensors in a well-controlled manner. The examples described in this chapter show clearly the potential of these materials and devices to significantly impact disease diagnosis, genetic screening, and drug discovery, as well as offering powerful new tools for research in many areas of disease diagnosis and life sciences.

Nonetheless, there are several challenges that still need to be met to further realize the capabilities of this technology. First, one fundamental challenge to the ultrasensitive detection is to synthesize well-defined NW structures with controlled atomic compositions and heterojunctions. In particular, the desired uniformity in miniaturized material structures with nanoscale abruptness has not been fully accomplished by

current synthetic methods and technologies. Second, despite the continuous efforts to enhance the sensitivity limit, the existing methods are still not sufficient to be applied in larger and more complex NW sensor arrays, in the same level of complexity similar to the optical detection platform such as gene microarrays. Third, the exquisitely powerful sensor systems designed for whole blood/serum detection still needs substantial development and optimization. Fourth, almost all the NW FET-based sensors are exclusively surface-bound devices. For the clinical application of NW biosensor devices, it is also critical to explore the transformation from on-chip signaling to in vivo human body testing.

In the next decade, continued efforts to achieve the capability in controlling the mechanisms of the NW sensor arrays will move beyond current technologies and take advantage of information emerging from genomics and proteomics to improve the diagnosis and treatment of cancer and other complex diseases. We believe that these advances can be developed at the commercial level in simple NW sensor devices that would represent a clear application of nanotechnology and, more importantly, a substantial benefit to society.

Acknowledgements

A.Z. and G.Z. thank the following funding agencies for supporting this work: the National Key Basic Research Program of China (2013CB934104), the National Science Foundation of China (21322311, 21473038), the Science and Technology Commission of Shanghai Municipality (14JC1490500), the Doctoral Fund of Ministry of Education of China, the Deanship of Scientific Research of King Saud University (No. RG#1435-010), and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning. A.Z. specially thanks the support of Hui-Chun Chin & Tsung-Dao Lee Chinese Undergraduate Research Endowment.

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Hybrid semiconductor/plasmonic nanowires for nanoscale photonic devices

18

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18.1 Introduction

A surface plasmon (SP) is a collective oscillation wave of free electrons along a noble metal (Au, Ag, Pt, etc.) surface (Barnes, Dereux, & Ebbesen, 2003; Berini & De Leon, 2012; Hutter & Fendler, 2004; Maier & Atwater, 2005; Maier et al., 2001; Muhlischlegel, Eisler, Martin, Hecht, & Pohl, 2005; Ozbay, 2006; Prodan, Radloff, Halas, & Nordlander, 2003; Stockman, 2011; Xia & Halas, 2005). SPs have unprecedented capability to concentrate light into a deep subwavelength regime through storing the optical energy with electron oscillations and further tailoring the light–matter interaction in nanoscale. In the last two decades, the coupling between exciton and SP has attracted more and more attention. It opens new avenues to manipulate the optical properties of semiconductor nanostructures and holds important applications in the development of novel photonic and plasmonic nanodevices.

18.2 Plasmonic nanowire waveguide and plasmon–exciton interaction in plasmonic nanowires

Future integrated photonic circuits with high speed and large bandwidth could overcome the limits of electronic devices (Ebbesen, Genet, & Bozhevolnyi, 2008; Lal, Hafner, Halas, Link, & Nordlander, 2012; Lieber, 2003; Lieber & Wang, 2007; Li, Qian, Xiang, & Lieber, 2006; Pauzauskie & Yang, 2006; Sorger, Oulton, Ma, & Zhang, 2012; Wei & Xu, 2012; Yan, Gargas & Yang, 2009). Although semiconductor-based optical devices have great potential, the light diffraction limit is a big obstacle in large-scale integration of photonic circuits. One possible solution is the use of metallic materials, in which plasmonic behaviors represent a kind of nanophotonics beyond the diffraction limit.

SPs describe the collective oscillation of conduction electrons in a metal surface, leading to enhanced electromagnetic fields confined at subwavelength nanoscale, which enables the manipulation of light beyond the diffraction limit (Gramotnev & Bozhevolnyi, 2010; Schuller et al., 2010). There are two types of SPs. For a metal–dielectric interface, SP mode represents a longitudinal surface charge density wave and can propagate

along the surface, which is often termed surface plasmon polaritons (SPPs). For metal nanoparticles (NPs) and nanostructures with finite size, the conduction electrons exhibit collective oscillation confined to a finite volume coherently in response to the electric field of incident light, known as localized surface plasmons (LSPs).

18.2.1 Surface plasmon polariton waveguiding in subwavelength metal nanowires

For one-dimensional metallic nanowires (NWs) with subwavelength diameter, SPPs propagate along the longitudinal direction, at the interface between the metal and the dielectric medium. Electric fields are highly localized at the surface and decay exponentially along the direction perpendicular to the surface, from the interface into the dielectric and metal volume both. The decay length into the vacuum is on the order of half of the wavelength of light. The decay length into the metal is the skin depth (<50 nm for Au and Ag). That means the light traveling is highly confined.

Because the wave vector of SP is larger than that of the free space light, direct excitation of SPPs in metal film by light is not possible. The conventional excitation of SPPs is a prism-coupled Kretschmann configuration, which can be also used to launch propagating plasmons in metal NWs (Figure 18.1(a); Allione, Temnov, Fedutik, Woggon, & Artemyev, 2008). For NWs, there is a special excitation method shown in Figure 18.1(b). When laser light is directly focused on the NW's end, the propagating plasmon can be excited by tip-scattering to satisfy the wave vector matching requirement (Ditlbacher et al., 2005). Similar to NW end-scattering, some other discontinued point, such as NP attachment, kink, and defect, can enable the conversion from photons to propagating plasmons by scattering (Knight et al., 2007). Figure 18.1(c) shows that traveling light in a tapered optical fiber can convert into metallic NWs as SPPs by near-field coupling (Dong et al., 2009; Guo et al., 2009; Wang, Yang, Fan, Xu, & Wang, 2011; Yan, Pausauskie, Huang, & Yang, 2009). Bharadwaj et al. demonstrated a direct conversion from electrons to plasmons, through a process of tunneling electrons to gap plasmon and then to propagating plasmons (Figure 18.1(d); Bharadwaj, Bouhelier, & Novotny, 2011).

When an SP is excited from one end, the SP can propagate along the NW and scatter out from the other end, as shown in Figure 18.2(a). The metallic NWs act as Fabry–Pérot (F–P) SP resonators where the propagation SP could be reflected by the NW end and interfere with the incident SPs. The scattered light intensity is modulated as a function of wavelength, with the distinct line shape of F–P resonant modes (Figure 18.2(b); Ditlbacher et al., 2005).

The propagating SPs sustain losses, including intrinsic Ohmic losses (Joule losses) and scattering losses (radiative losses). The Ohmic loss is originated from the crystal lattice scattering of free electron and the energy is converted to heat. The SPs lose energy as well through the end-scattering and emission as photons. The scattering losses also happen at the defect points like surface roughness. The losses determine the propagating distance of plasmon in NWs. Figure 18.2(b) compares the plasmon propagating in a single crystalline silver NW by chemical synthesis and a polycrystalline

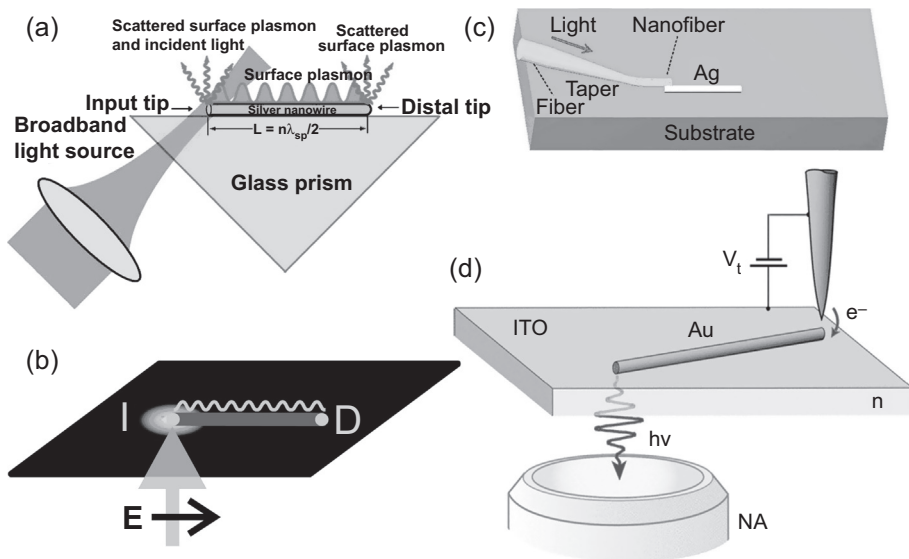


Figure 18.1 Plasmon excitation in metallic NWs. The excitation of SPPs in NWs by (a) Kretschmann configuration (Allione et al., 2008), (b) direct illuminating on the NWs distal (Ditlbacher et al., 2005), (c) fiber coupling (Guo et al., 2009), and (d) electrical excitation (Bharadwaj et al., 2011).

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NW by lithographical fabrication. The high-quality modulation in the single crystalline NW indicates that highly ordered crystalline structure sustains less plasmon losses and achieves a large SP propagation length.

Besides crystalline structure, the excitation and propagation behaviors of SPs in metallic NWs are dependent on some other parameters, such as incident light polarization, SP resonant wavelength, NW diameter, and surrounding medium (Figure 18.2(c)–(f); Li, Bao, Fang, Guan et al., 2010; Li, Bao, Fang, Huang et al., 2010; Ma et al., 2010). Compared with perpendicular polarization, incident light with polarization parallel to NWs could be highly coupled into SP, especially for the NWs with small diameter. For plasmon propagating, the propagation length is longer for the NWs with large diameter and the plasmons with long wavelength.

18.2.2 Surface plasmon networks, logic gates, and communications

For a silver NW cross or network, the propagating SP along the NW could couple to other NWs or scatter to free space distally. The coupling and scattering efficiency are related to the excitation polarization. It is possible to realize the logic gates, photonic circuits, and information processing (Figure 18.3).

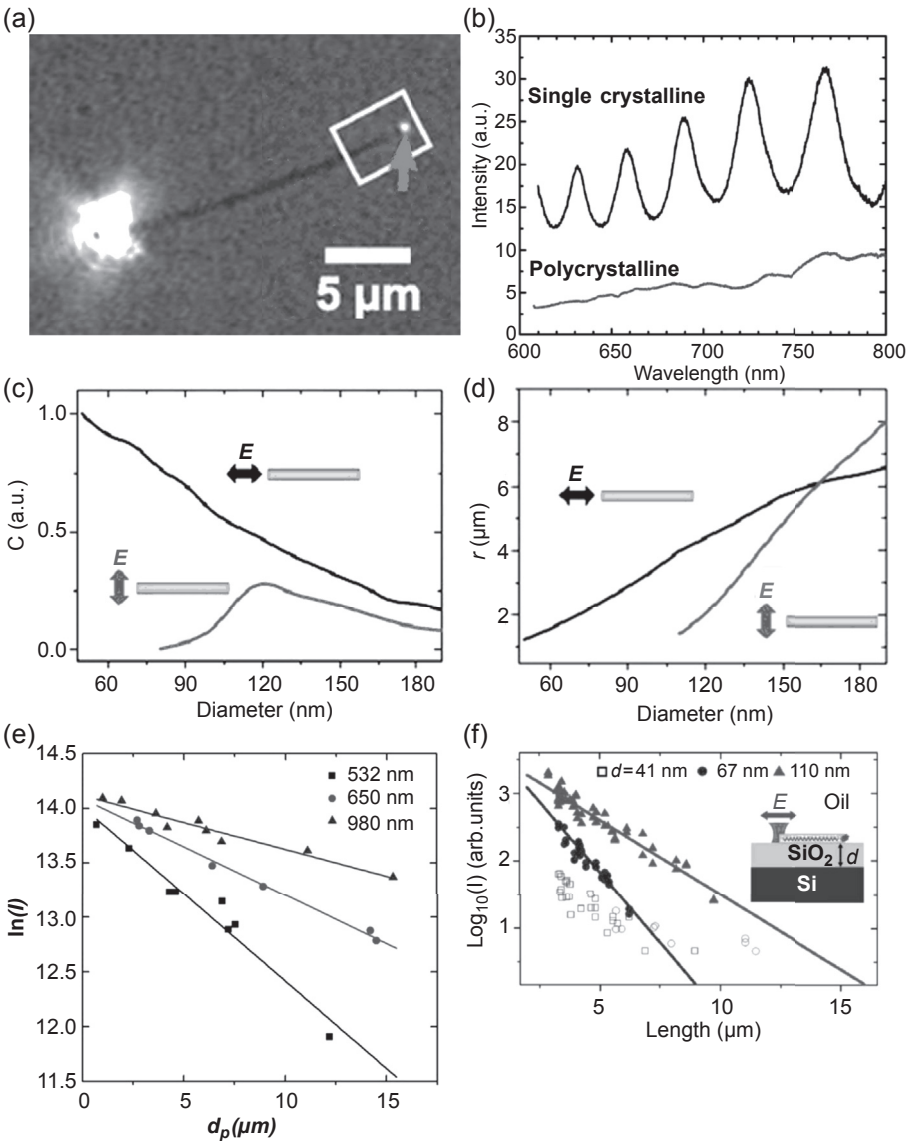


Figure 18.2 Plasmon propagating properties in metallic NWs. (a) Microscopic image of a silver NW, in which the plasmon is excited by a focused laser on one end (bright spot on the left), propagated along the NW, and scattered out from the other end (arrow on the right) (Ditlbacher et al., 2005). (b) Scattered light spectra from the distal NW end of the chemically fabricated wire (single crystalline, upper curve) and the lithographically fabricated wire (polycrystalline, lower curve) (Ditlbacher et al., 2005). (c) The in-coupling efficiency C and (d) the $1/e$ damping length r for two SPPs modes as a function of the wire diameter (Li, Bao, Fang, Huang et al., 2010). (e) The log of tip emission intensity as a function of propagation distance at the wavelength of 532, 650, and 980 nm (Yan, Pausauskie et al., 2009). (f) Emission intensities from

Sanders et al. found that SP propagation modes can couple between overlapping NWs (Sanders et al., 2006). When SP in one NW is excited by a focused laser on the end, radiation is emitted at the intersection and from ends of the other NW. Fang et al. investigated the polarization-dependent SP coupling and emission of two NWs (Fang et al., 2010). The results show the SP can be routed into different NW by controlling the polarization of the incident laser light. The routing behavior is strongly dependent on the wavelength of light. Wei et al. demonstrated an SP-based interferometric logic by an NW network with two input terminals (Wei, Li et al., 2011). SPs were launched into two input terminals by polarization laser beam with a different phase. The emission intensity at output terminals was controlled by the phase difference, resulting in oscillatory behaviors with a large dynamic range. The intensities can be assigned ON and OFF states. By choice of relative phase and input polarization, this branched NW can function as a logic circuit. More complex logic functions can also be realized using branched NWs with two or more branches (Wei, Wang, Tian, Kall, & Xu, 2011). The propagating SP could also couple to NPs and exhibit remote excitation of surface-enhanced Raman spectroscopy (SERS) (Fang, Wei, Hao, Nordlander, & Xu, 2009). This result shows the potential for NW SPPs to propagate information in larger, more complex nanoscale optical systems.

18.2.3 Exciton–plasmon interaction in plasmonic NWs

When a nanoscale optical emitter (semiconductor quantum dot (SQD), dye, etc.) locates near a plasmonic NW, the emission properties of emitter will be significantly modified. The strong near-field exciton–plasmon interaction includes the following: (1) the radiative decay rate to the free space of emitter can be modified by the plasmon, (2) the exciton energy can nonradiatively transfer to metal and damp, and (3) the radiative energy can be coupled and transferred to plasmon modes in NW (Akimov et al., 2007; Chang, Sorensen, Hemmer, & Lukin, 2006; Chang, Sorensen, Hemmer, & Lukin, 2007).

The excitation and detection of single photon and single plasmon is the attractive problem in quantum science and is of interest for the applications of single-photon switching, quantum information, etc. Akimov et al. reported emission from a single SQD optically excited in close proximity to a silver NW coupled directly to SP in NW and lighted up from the NW's end (Figure 18.4(a); Akimov et al., 2007). A single SQD could only emit a single photon at a time, and the single photon could either radiate into free space or couple to NW, forming single, quantized plasmons.



NWs on layered substrates with different silica layer thicknesses ($d = 41, 67$, and 110 nm) as a function of NW length L . Incident light is 633 nm wavelength and polarization parallel to the NW (Li, Bao, Fang, Guan et al., 2010).

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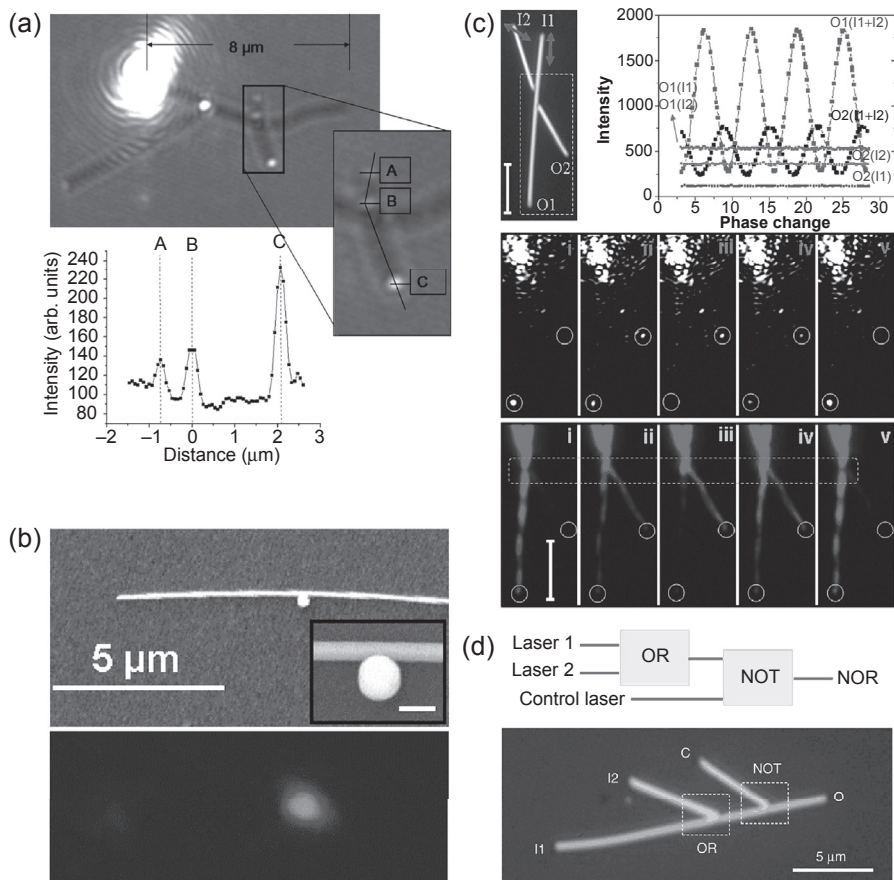


Figure 18.3 Surface plasmon networks, logic gates, and communications. (a) Surface plasmon coupling and fan out in plasmon NW networks (Sanders et al., 2006). (b) SERS could be remotely excited by plasmon propagating in metallic NW. The lower image is the Raman image (at the Raman peak of 436 cm^{-1}) after background subtraction of fluorescence. The laser spot ($2\text{ }\mu\text{m}$) is at the left end of the NW and the strong SERS signal from the wire/particle junction is obtained (Fang et al., 2009). (c) Surface plasmon-based interferometric logic could be realized by an NW network with two input terminals (Wei, Li et al., 2011). (d) Logic gate NOR built by cascaded OR and NOT gates in designed NWs network (Wei, Wang et al., 2011).

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Fedutik et al. also demonstrated an exciton–plasmon–photon conversion in a CdSe/SiO₂/Ag-NW system (Fedutik, Temnov, Schops, Woggon, & Artemyev, 2007; Fedutik, Temnov, Woggon, Ustinovich, & Artemyev, 2007). They found the optimal distance between SQD and Ag NW for SQD spontaneous emission rate enhancement was 15 nm. The plasmon propagation length in NW is dependent on the wavelength,

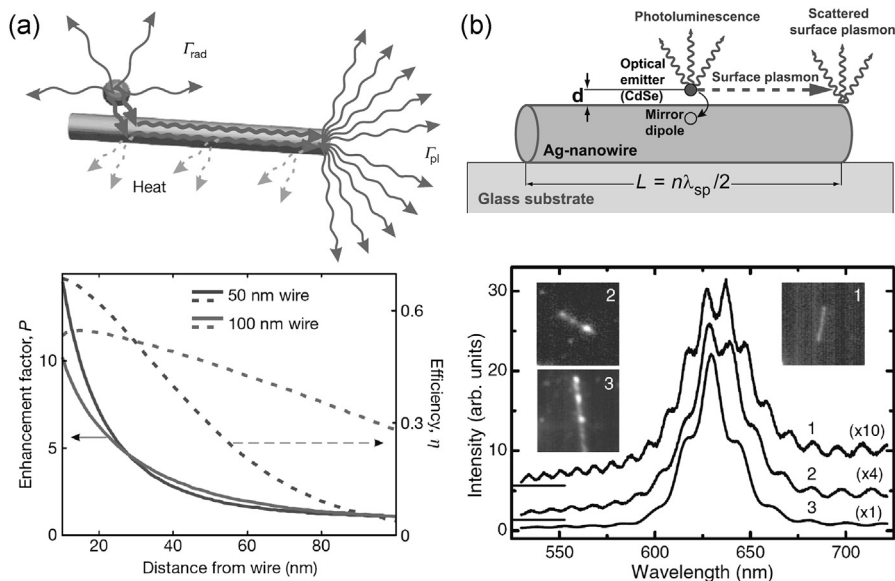


Figure 18.4 Coupling between surface plasmon and nanoemitter. (a) Coupled SQD can either spontaneously emit into free space or into the guided surface plasmons of the NW. The enhancement factor P (solid line) and efficiency of emission into surface plasmons (dashed line) are dependent on the distance of the emitter from the NW edge (Akimov et al., 2007).

(b) Exciton–plasmon–photon conversion in SQD–NW nanosystem. Nanocrystal emission spectra modulated by the silver nanocavity modes measured for silver wires of different length L and a SiO_2 shell of $d = 10\text{--}15\text{ nm}$ (Fedutik, Temnov, Schops, et al., 2007).

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and the end-emission spectra are modulated by standing wave modes in the plasmon cavity (Figure 18.4(b)).

The emission rate coupled to SP is proportional to $1/R^3$. One can gain a very strong SP coupling through reducing R , but the SP propagation losses are also significantly increased. An interesting way to solve this problem is using a pair of NWs, which can lead to stronger exciton–plasmon coupling and smaller losses of SP propagation (Figure 18.5; Liu, Cheng, Yang, & Wang, 2008). Compared with a single NW, the coupled energy into plasmons can be increased by four times when the distance between dipole emitter and Au NW surface equals 15 nm. The far-field scattering intensity is also increased by four times.

The coupling between propagation plasmon and nanoemitter can also exhibit interesting transportation properties, which could be used as plasmonic devices in optical communication and quantum information processing. The theoretical investigation shows that coupling between a single plasmon and SQDs could modulate the transportation of plasmon in 1D SP waveguide, as Figure 18.6 shows (Kim, Li, Yang,

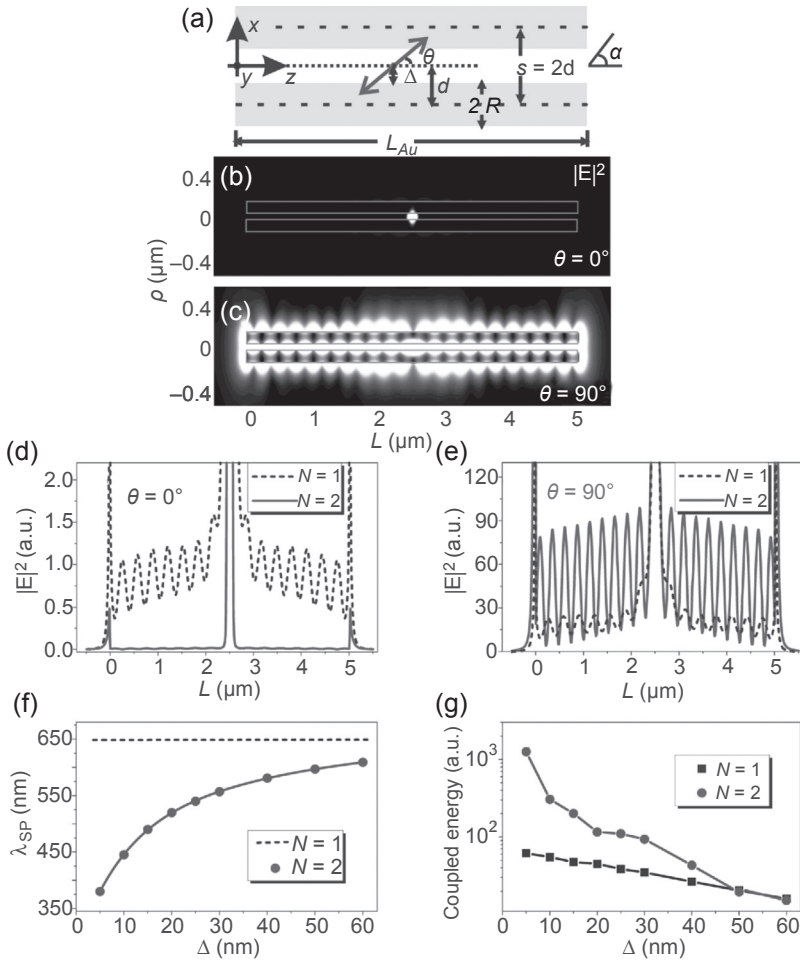


Figure 18.5 Enhanced coupling efficiency between exciton and plasmon by a pair of NWs [Liu et al. \(2008\)](#). (a) Schematic of an emitter coupling to a pair of Au NWs. (b) $|E|^2$ distributions with emitter polarization $\theta = 0^\circ$, and (c) $\theta = 90^\circ$. (d) $|E|^2$ distributions along Au NW surface near the emitter with $\theta = 0^\circ$, and (e) $\theta = 90^\circ$ for a single (dashed curves) and a pair of NWs (solid curves). (f) λ_{SP} as a function of emitter-NW distance Δ for $N = 2$ (solid circles) and $N = 1$ (dashed line) when $\theta = 90^\circ$. (g) The power coupled in the NW P_{SP} in one Au NW versus Δ for emitter coupling to a pair of NWs (solid circles) and a single NW (squares). Adapted with permission from [Liu et al. \(2008\)](#). Copyright (2008) The Optical Society of America.

[Hao, & Wang, 2010](#)). The transmission of the single plasmon can be switched on or off by dynamically tuning the transition energies of the two SQDs and the distance L between two SQDs. For example, when the transition energy of SQDs is resonated with the SP, the plasmon is completely reflected and the two-SQD system behaves as a mirror. However, when the frequency of the incident plasmon is set between

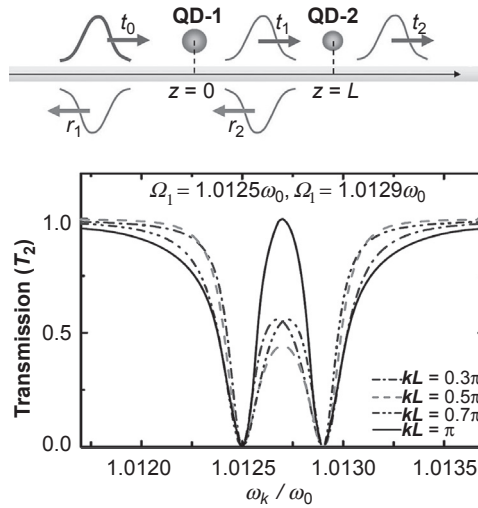


Figure 18.6 Modulation of plasmon transportation by exciton–plasmon interaction (Kim et al., 2010). Top: Schematic diagram of a system consisting of a single plasmon and two SQDs coupled to a metal NW. t_i and r_i are the transmission and reflection amplitudes at the place z_i , respectively. Bottom: Transmission spectra of a propagating plasmon interacting with two SQDs for different phases (distances). The transmission of plasmon (ω_k) could be switched on or off by adjusting transition energies (Ω_1 and Ω_2) and controlling spatial separation (L) of the two SQDs. Adapted with permission from Kim et al. (2010). Copyright (2010) AIP Publishing LLC.

the two transition frequencies, the complete transmission peaks appear at $kL = n\pi$ ($n = 0, 1, 2, \dots$).

The metal NW arrays have special plasmon properties compared with a single NW (Kabashin et al., 2009; Kawata, Ono, & Verma, 2008; Ono, Kato, & Kawata, 2005; Pollard et al., 2009; Wurtz et al., 2011). Strong coupling between the nearby metal NWs induces the generation of standing waves in the plasmonic cavities and the formation of epsilon-near-zero plasmonic metamaterials. The Au NW array exhibits a highly efficient multiphoton avalanche photoluminescence (PL) (Gong, Zhou, Xiao, Su, & Wang, 2008; Wang et al., 2007). The plasmonic Fano resonance is found in a hybrid system consisting of an NW array and NP percolating film (Zhou et al., 2011). The strong plasmonic coupling and interference in this hybrid system bring about a nonlinear enhancement effect. The transmittance of the percolating Au film is enhanced $\sim 55\%$ by the Au NW array (Figure 18.7(b)). Conversely, the local field in the Au NW array is enhanced as well, leading to over 10^2 times the enhancement of the PL (Figure 18.7(a)).

One problem to be solved in the development of nanoscale photonic devices is to control the propagation direction of light efficiently. A plasmon NW array could be a candidate for the photonic devices. The optical nanoemitters can be efficiently coupled to metal NWs with a large Purcell factor (Akimov et al., 2007; Chang et al., 2006, 2007; Nan et al., 2014; Zhou et al., 2010; Zhou, Su, Peng, & Zhou, 2008). In addition, they can generate subwavelength images of those nanoemitters at the opposite ends of

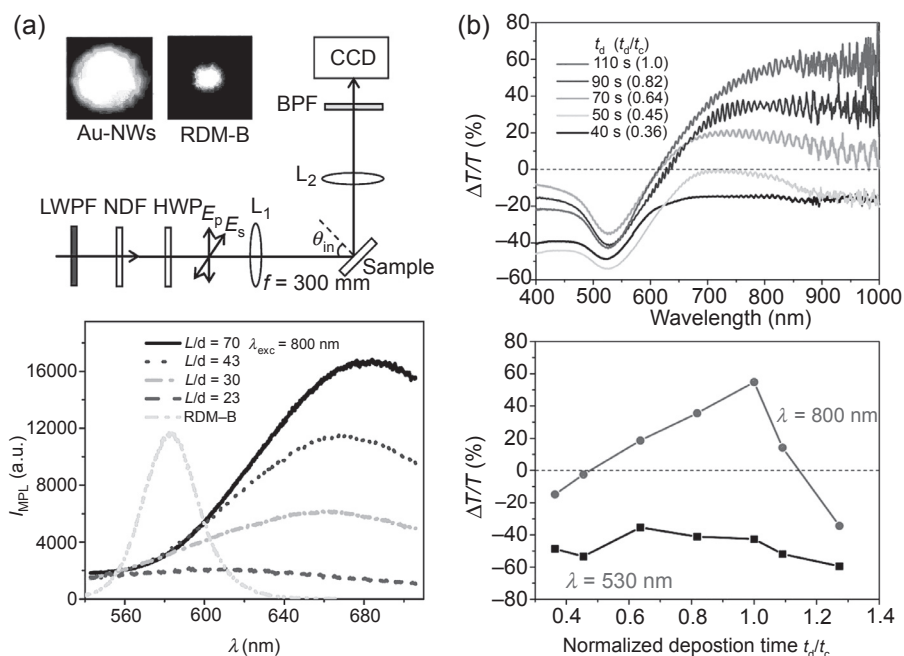


Figure 18.7 Multiphoton avalanche luminescence and Fano resonance-induced transmission enhancement of metallic NW array. (a) Visible multiphoton PL (MPL) photos and spectra from ordered-arrayed Au NWs and reference sample rhodamine B (RDM-B). Illustration of the optical setup for excitation and recording MPL spectra. The excitation intensity and recording conditions for two photos are the same. The center peak of MPL of ordered-arrayed Au NWs shifts from 600 to 680 nm as the aspect ratio L/d increases from 23 to 70 (Wang et al., 2007). (b) Normalized difference of the transmittance ($\Delta T/T$) of the Au films with and without an Au NW array. The growth time of the Au NWs is fixed at 40 s. The sputtering deposition times (t_d) of the Au films are 40, 50, 70, 90, and 110 s, respectively. $\Delta T/T$ (at the wavelength of 530 and 800 nm) as a function of the normalized deposition time t_d/t_c ($t_c = 110$ s). The transmission at 530 nm is inhibited in the whole deposition time region. In contrast, the transmission at 800 nm is significantly enhanced ($\Delta T/T$ reaches about +55%) when $t_d/t_c = 1.0$ (Zhou et al., 2011). Adapted with permission from Wang et al. (2007), Zhou et al. (2011). Copyright (2007 and 2011) American Chemical Society.

the NWs due to a focusing effect, while the radiative energy transfer exhibits a higher efficiency and improved directionality (Zhou et al., 2010).

The excitation energy of nanoemitters can be efficiently converted to the SPs through strong coupling near the tips of the Ag NWs. Both SQDs located at the top and in the middle of the two NWs are efficiently coupled to the long-axis SP resonance, as shown in Figure 18.8(a). When a point source is located at the central axis of an NW, only z -polarized source can be strongly coupled to the NW array via excitation of LSP resonances. After resonant transmission through the NW array, the subwavelength images of the point sources are generated at the output side (right

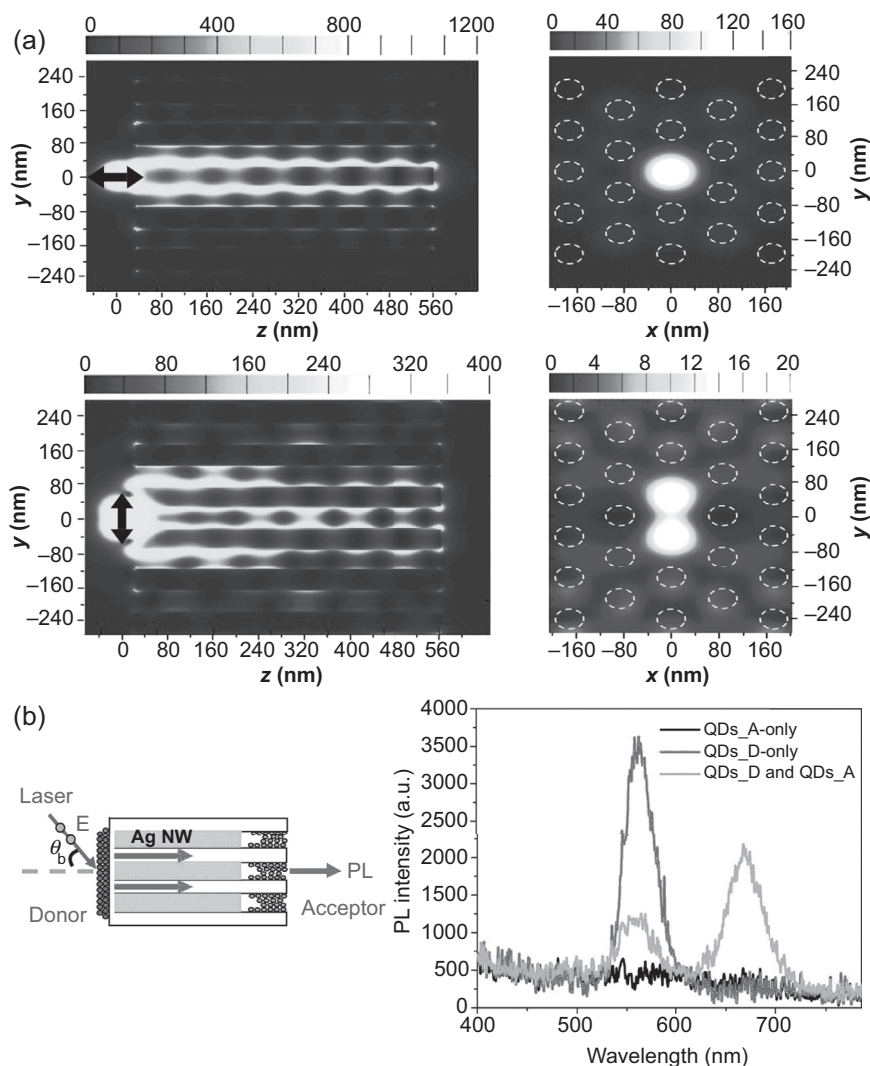


Figure 18.8 Coupling between an SQD dipole with metal NW array and radiative energy transfer between semiconductor SQDs (Zhou et al., 2010). (a) Seventh harmonic half-wave plasmon resonances of the Ag NW array ($x = 0$, YOZ plane) and the subwavelength imaging ($z_{\text{out}} = 24$ nm, XOY plane) of a z -polarized point source at the center of an NW and a y -polarized point source at the middle of two NWs. The diameter and length of NWs are $d = 50$ nm and $L = 540$ nm, respectively. The array period is $a = 100$ nm. (b) Radiative energy transfer between the SQDs across the Ag NW array. The illustration shows the sample structure with Ag NWs grown in the AAO template, the donor SQDs (QDs_D) absorbed on the surface of the Al_2O_3 barrier layer, and the acceptor SQDs (QDs_A) deposited in the rest of the nanopores of the AAO template. The PL spectra show the PL of donor-only, the acceptor-only, and the donor–acceptor samples. The emissions around 560 and 660 nm are attributed to the donor and acceptor SQDs, respectively.

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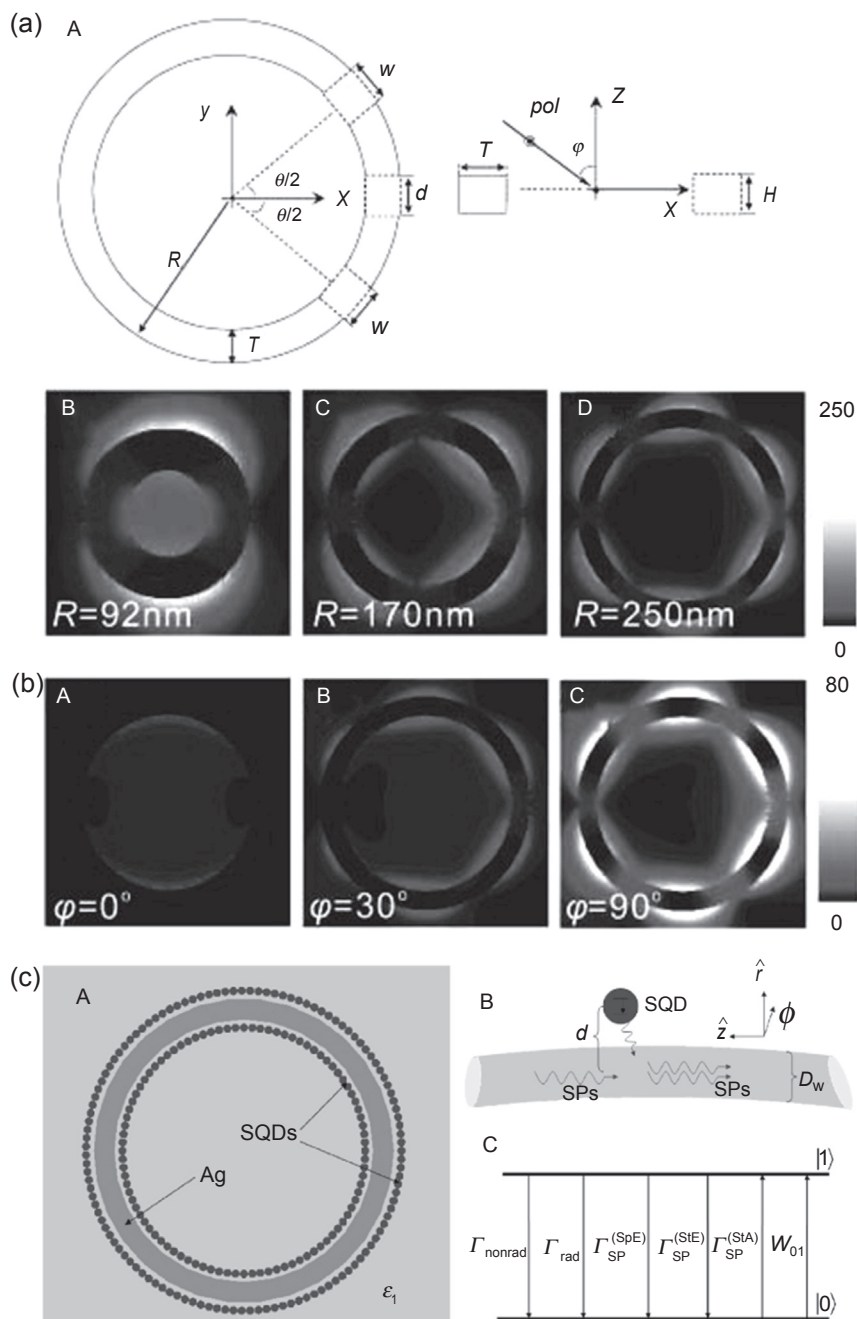


Figure 18.9 Plasmon excitation and amplification in nanorings. (a), (b) Simulations of multi-pole plasmon resonances and plasmon propagation in Au nanorings. I distributions for perfect nanorings (a) with outer radius $R = 92, 170, 250$ (the incident angle is fixed at $\varphi = 85^\circ$)

end) of the array due to the near-field imaging effect. Interestingly, a y -polarized source is more efficiently coupled to the NW array than a z -polarized source when it is located in the middle of two NWs, and two subwavelength images are generated around two NWs in this case.

Metallic NW arrays could act as plasmonic waveguides with high efficiency and directionality for the radiative energy transfer between SQDs. As shown in Figure 18.8(b), the donor SQDs and acceptor SQDs are assembled on the two sides of Ag NW arrays with a length of ~ 560 nm. An s -polarized laser with a wavelength of 400 nm is slantwise incident to the input side (with donor SQDs) of the devices. The acceptor SQDs on the output side cannot be excited because the excitation laser is completely blocked by the Ag NW array. The energy can be transferred from the excited donor SQDs to the acceptor SQDs through a conversion process of exciton—plasmon—exciton—photon with higher conversion efficiency compared to single NW and longer transmitting distance compared to the Ag film. The detail processes include efficient exciton—plasmon conversion at the input side of the array through near-field strong coupling, directional wave guidance, and resonant transmission via half-wave plasmon modes of the NW array; subwavelength imaging at the output side of the array; and finally converting the excitation energy from the images of the donors to the acceptors. From the experimental data, the energy transfer efficiency is calculated to be about 0.7, which means that 70% of the energy transmitted through the Ag array is coupled to the acceptors. The energy transfer efficiency can be further improved by fine-tuning the wire length and decreasing wire length variation.

A nanoring is a special plasmonic NW cavity in which the two ends of NW connect to form a closed plasmonic cavity (Aizpurua et al., 2003; Hao, Larsson, Ali, Sutherland, & Nordlander, 2008; Nordlander, 2009). Theoretical simulation shows that multi-pole resonances, as so-called dark plasmons, could be excited in nanorings (Liu, Zhang, & Wang, 2009). As shown in Figure 18.9(a) and (b), with normal excitation, only dipole exists and the local field enhancement is very weak. With slant excitation, multipolar plasmons are excited, and the field enhancement increases with the increase of incident angle φ . The SP propagation is involved in the multipolar plasmon excitation. It is found that the field enhancement on the right side is much stronger than the left side under oblique incident excitations. It can be understood that there are SP propagation processes for $\varphi > 0$, and the energy is focusing to the right side.



and (b) with incident angle of $\varphi = 0^\circ, 30^\circ, 90^\circ$ (the outer radius is fixed at $R = 250$ nm). The excitation wavelength is 800 nm. The thickness and height of nanorings are $T = 45$ nm and $H = 30$ nm, respectively (Liu et al., 2009). (c) Stimulated emission amplification in metallic nanoring by using SQDs as gain medium. An Ag nanoring is surrounded by SQDs. The nanoring and SQDs are embedded in a dielectric with electric permittivity ϵ_1 . The SPs in the Ag nanoring could be amplified through the strong coupling of exciton and plasmon. The schematic of stimulated emission and the energy-level diagram of a two-level SQD are shown. $|1\rangle$ and $|0\rangle$ are excited and ground states of the SQD, respectively (Yang et al., 2010).

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The standing waves of SPs supported by nanorings are free from the end-loss of SPs in NWs, which indicates that nanorings could act as an ideal plasmonic nanocavities. As shown in Figure 18.9(c), in a nanosystem consisting of an Ag nanoring and the surrounding active SQDs, the amplification of propagating SPs in Ag nanorings could be achieved through the strong coupling of exciton and plasmon (Yang et al., 2010). Numerical calculations show that when the pumping rate of SQDs is larger than the pumping threshold, at first the SP number increases quickly within a short propagating length, and then becomes saturated after a long propagating distance. The saturated or maximum value of the SPs number per unit length is linearly dependent on the pumping rate.

High-quality silver nanorings can be chemically grown in a reductive reaction solution with magnetic stirring by using the polyol method (Gong et al., 2009). The silver nanorings have a perfect ring shape, smooth surface, and circular cross-section (Figure 18.10(a)). Structure characterization indicates that the silver nanorings are singly twinned crystals (Figure 18.10(b); Zhou et al., 2009). This means that this kind of silver nanoring is a perfect plasmon cavity with small propagation losses. The multipolar dark plasmons in the nanoring are excited with slantwise excitation, and the local field around the silver nanoring is strongly confined and enhanced at the special positions even though the silver nanoring has a central-symmetric shape and a smooth surface. Strongly focused scattering in the nanoring can be seen, and the focus spot moves to the far side of the nanoring. The scattering focus position and intensity are related to the incident angle, excitation wavelength, and polarization (Figure 18.10(c) and (d); Zhang et al., 2010; Zhou et al., 2009).

As a kind of optical nanoantenna, silver nanorings have unique local field confinement and enhancement. To demonstrate the enhancement of PL from quantum emitters by silver ring-nanoantenna, a monolayer of CdSe/ZnS SQDs were self-assembled on the quartz glass substrate by electrostatic interactions, and then the silver nanorings were dropped onto the separation layer. Figure 18.11(a) shows the spatial distribution of PL from a monolayer CdSe/ZnS SQDs enhanced by a single silver nanoring with incidence angle 60° and 82° . One can see that the PL intensity is significantly enhanced around the cross-points of the incident plane and nanoring. These two cross-points are called the “hot spots” of the silver-ring nanoantenna. The PL enhancement at the right hot spot is stronger than that at the left hot spot due to the focus effect of the nanoring. The largest value of enhancement in the SQDs-nanoring system is 7.3. This large relative enhancement factor $I_{\text{hot}}/I_{\text{mid}}$ of the silver nanoring may be attributed to three reasons: (1) a large local field enhancement on the hot spot at the excitation wavelength, which is assisted by the focus effect of the whole silver nanoring; (2) plasmon-enhanced radiative decay rate of the exciton at the emission wavelength; and (3) SPs around whole nanorings probably propagating toward and emitting out from the hot spot when the excitation is strong enough.

Further experiments demonstrate that the hot spots position of the silver ring could be tuned by the wave vector of the incident laser (Figure 18.11(b)). This multiple hot-spots technique could be used to investigate the coupling of SQDs by plasmon propagating in a silver nanoring.

18.3 Coupling between semiconductor nanowires and surface plasmons

One-dimensional semiconductor NWs are widely studied in sciences and technologies for their unique optical and electric properties, such as serving as an efficient optical waveguide, high-gain medium, electronic conductor, etc. The semiconductor NWs bridge the gap between nanoscale and microscope, and are good candidates as building blocks for electric and photonic nanodevices. The performances of the NW-based electric and photonic devices are mainly determined by the properties of excitons (generation, transport and recombination, etc.), which is one of the most important elementary excitations in the semiconductors. As introduced in the previous parts, SPs can enhance the efficiency of light absorption and scattering, tailor the recombination process of excitons nearby using the strong localized field, and mediate the energy transfer with excitons via dipole–dipole interaction. Recently, many efforts have been devoted to investigate the interaction between semiconductor NWs and metal nanostructures such as NPs (Chen et al., 2012; Lee, Govorov, Dulka, & Kotov, 2004; Lee, Hernandez, Lee, Govorov, & Kotov, 2007; Lee et al., 2006; Peng et al., 2010), core–shell NWs (Cho et al., 2011; Cho, Aspetti, Park, & Agarwal, 2013), films (Lu et al., 2012; Oulton et al., 2009; Sorger et al., 2011), etc., and then manipulate the optical, opto-electric, and cavity properties of semiconductor NWs.

18.3.1 Plasmon-enhanced optical process in semiconductor nanowires

Metallic NP-decorated semiconductor NWs are very promising in a wide range of applications related to NWs. It has been widely reported that the PL and Raman intensities of semiconductor NWs can be greatly enhanced in the proximity of metal NPs.

Figure 18.12 shows a hybrid nanostructure made from CdTe NWs and Au NPs, in which the Au NPs were decorated by using the conjugation of biotin and streptavidin and formed a dense shell around the CdTe NWs (Lee et al., 2004). The diameter of the CdTe NWs and Au NPs are 5.8 ± 1.1 and 3.7 ± 0.3 nm, respectively. The distance between the Au NPs and CdTe NWs are about 10 nm. Even at such a long distance, the PL of Au NP-conjugated CdTe NWs is enhanced by five times as well as a blueshift of the emission peak center wavelength as compared to bare CdTe NWs. The enhancement factor increases when there are more NPs attached, suggesting a relative long-range exciton–plasmon interaction between the CdTe NWs and Au NPs. An SP-induced total local field enhancement model was considered and well explained the experiment results including the enhancement factor. The excitation of SPs in the Au NPs increases the effective absorption of the CdTe NWs and the induced local electric field accelerates the radiative rate of the CdTe NWs (or Purcell effect), leading to the enhancement of semiconductor PL.

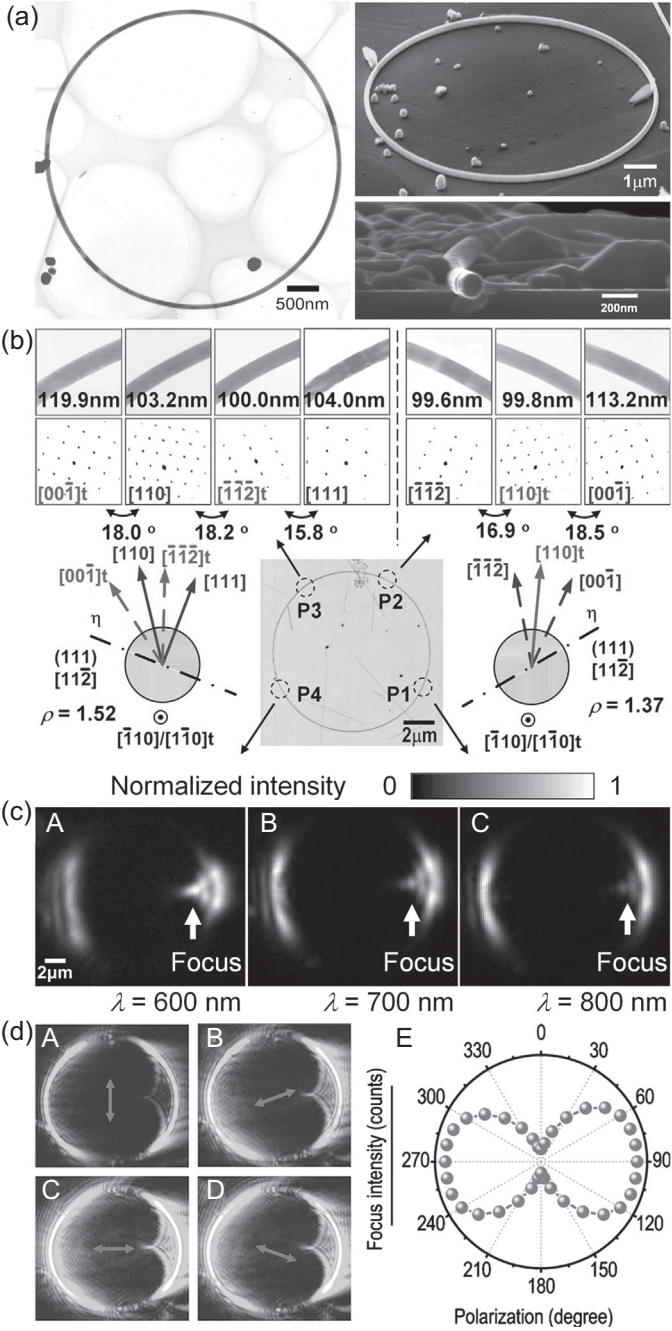


Figure 18.10 Synthesis, crystal structure, and scattering of Ag nanorings. (a) TEM and SEM images of chemical synthesized Ag nanorings (Gong et al., 2009). (b) Crystal characterization of silver nanorings shows that Ag nanorings are a singly twinned crystal structure with smooth

In addition to luminescence enhancement, the Raman scattering cross-section enhancement or so-called SERS, and further photocurrent were also observed in NW–NP hybrid system (Chen et al., 2012; Peng et al., 2010). Through decorating Ag NPs onto Si NWs, Peng et al. demonstrated a SERS enhancement factor of ~ 7 by single Ag NP due to an SP-induced local electric field, as Figure 18.13(a) shows. The Ag NPs are heteroepitaxially grown onto the Si NWs by a surface reduction mechanism. The SERS enhancement factor is sensitive to the incidence polarization: the Raman intensity is 10 times stronger as the excitation laser field is parallel to the NW axis than perpendicular polarization. The polarization-dependent behavior is mainly contributed to the NW antenna; however, a distortion of $10\text{--}15^\circ$ in polar plots compared to previous literature indicates an SP modified antenna effect. Furthermore, through adopting an Au dimer decoration, they further enhanced the Si Raman signal by 24 times. More importantly, the photocurrent of a single Si NW is increased by 100% by decorating the Au NPs (Figure 18.13(b)). The improved photosensitivity can be contributed to local field induced by SP resonance absorption of Au NPs (Chen et al., 2012).

With two flat end-facets serving as reflecting mirrors and semiconductor material as gain media, one-dimensional semiconductor NWs can be functioned as axial F–P cavities. Tailoring the optical gain and cavity mode in NW lasers is important for the development of high-performance nanoscale oscillators/amplifiers/lasers. Until now, there are a lot of methods to tune the NW cavity mode, which is mostly based on the modification of semiconductor band structure, such as electric field modulation, or alloying semiconductors. However, these methods have so far gained limited success in achieving output mode tunability of the NW laser due to the considerable optical losses. Recently, SPs have proved their capability to manipulate the NW cavity mode and further the lasing wavelength. Zhang et al. demonstrated that an Ag NP in the vicinity of a CdS NW can simultaneously modulate the effective cavity length, equivalent phase shift, and the Q factor of the cavity modes (Zhang et al., 2011). Ag NP acts as a reflective and half-reflective nanomirror when it is located at the end and at the side of the CdS NW cavity, respectively. When the CdS NWs is sitting on Au film with insulator SiO_2 thin layer as spacer, the Burstein–Moss effect inside the CdS NWs can be enhanced by the extremely confined electric field in the nanometer-thick insulator layer. The hybrid semiconductor–insulator–metal structures are well-known to support the low-loss SPP. The enhanced Burstein–Moss

surface and elliptical wire cross-section. The schematic illustrations of the cross-section exhibit the zone axes, twinning plane (η , dashdot line), and growth axis direction. The solid and dashed lines express the zone axes in different twin variants. ρ , estimated ellipticity of the cross-section (Zhou et al., 2009). (c) Silver nanorings exhibit unique focused scattering patterns with slanted illumination. The focused scattering is strongly dependent on excitation wavelength (Zhou et al., 2009). (d) Polarization-dependent far-field scattering images. The focus intensity and scattering pattern are also dependent on the excitation polarization (Zhang et al., 2010).

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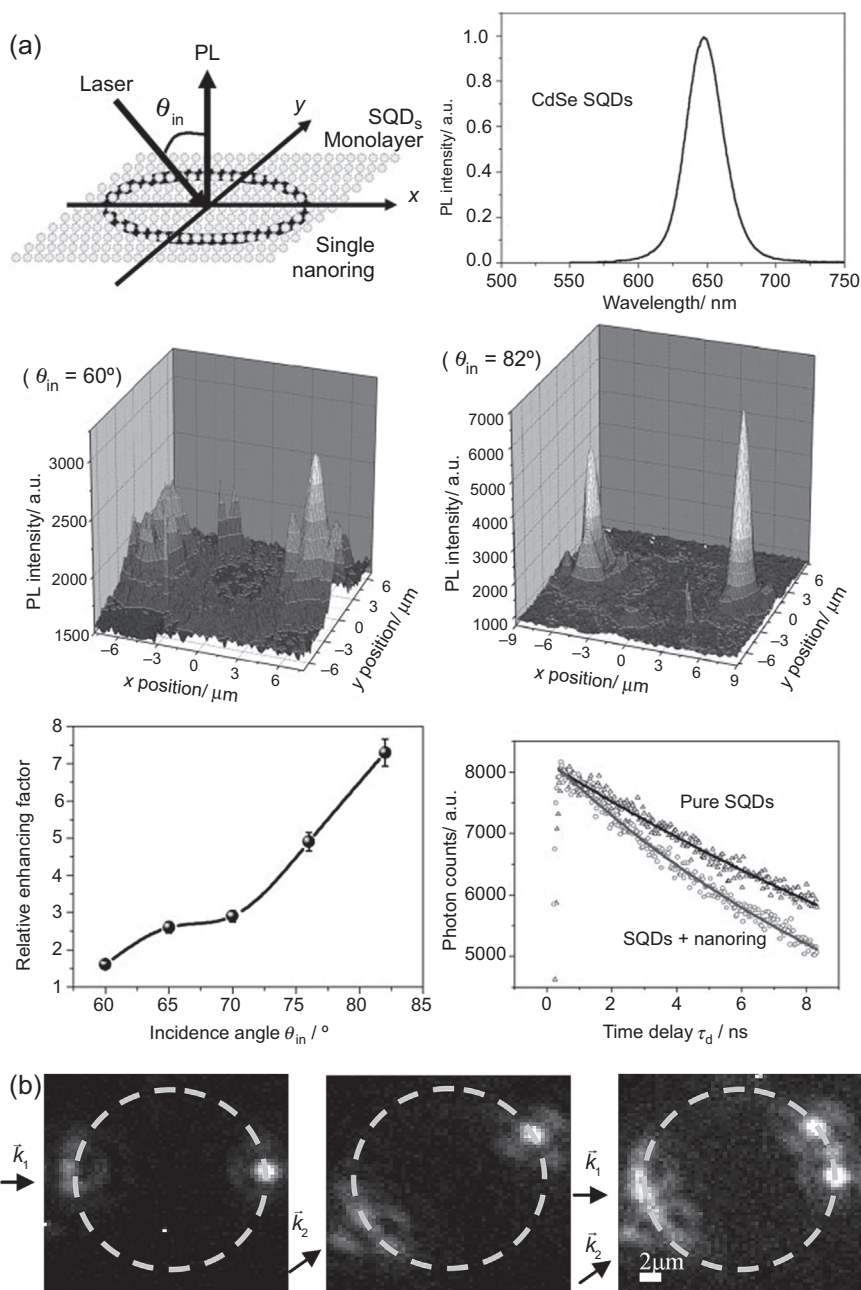


Figure 18.11 Enhanced exciton–plasmon interaction by silver ring-nanoantenna (Gong et al., 2009). (a) The illustration shows the nanosystem with a silver nanoring dropped on a monolayer of CdSe/ZnS SQDs. The emission wavelength of CdSe/ZnS SQDs is at 650 nm. The PL images with incident angle of 60° and 82° show that the PL intensity is significantly enhanced around two “hot spots.” The ratio of PL intensity at the hot spot and the other middle part on the silver nanoring (I_{hot}/I_{mid}) as a function of incident angle show the maximum enhancement factor that could be achieved is 7.3. The radiative decay rate of SQDs is enhanced by Ag nanoring.

(b) Tunable hot spots of the silver nanoantenna rings by incident wave vector.

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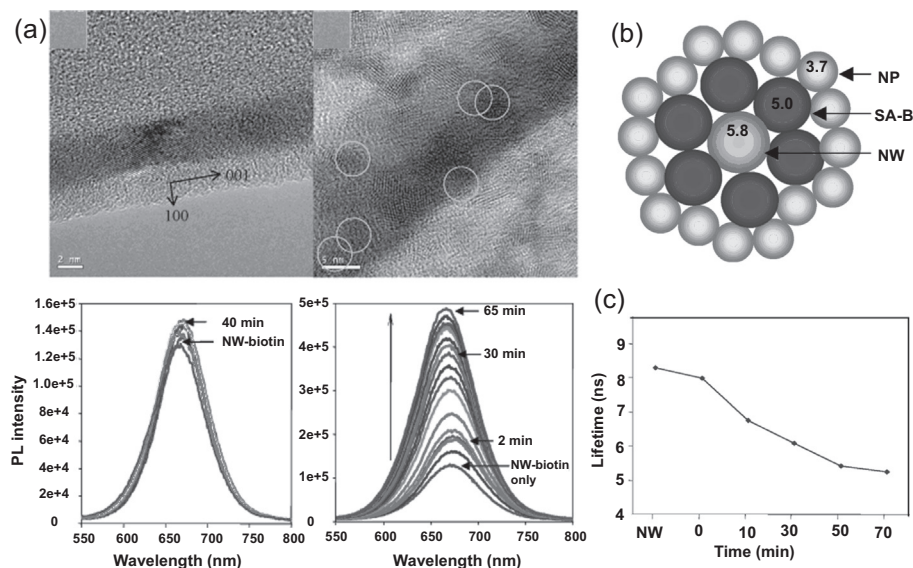


Figure 18.12 Surface plasmon-enhanced photoluminescence in semiconductor NWs (Lee et al., 2004). (a) Au NP are decorated onto CdTe NWs using the conjugation of biotin and streptavidin. The TEM images (upper panel) show that Au NPs form a dense layer surrounding the CdTe NWs. The diameter of the CdTe NW and Au NP are 5.8 ± 1.1 and 3.7 ± 0.3 nm, respectively. The photoluminescence intensity of CdTe NW increases with the Au NP-decorating process (bottom panel). The highest photoluminescence enhancement with Au NP is ~ 5 times. (b) The schematics of Au NP-CdTe NW core-shell structure. The distance between Au and CdTe NW is ~ 10 nm. Therefore the photoluminescence enhancement is due to long-range exciton-surface plasmon interaction. (c) The photoluminescence lifetime of CdTe NW decreases with the Au NP-decorating process.

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effect leads to a larger blueshift of the output photonic lasing wavelength of the CdS NWs. The enhancement factor increases with the decrease of SiO_2 thickness as a result of the increase of localized electric field and exciton-plasmon interaction strength. Through varying the thickness of SiO_2 from 100 to 5 nm, the lasing wavelength was tuned from 504 to 483 nm. Tunability of ~ 30 nm was obtained (Liu, Zhang, Yip, Xiong, & Sum, 2013).

More interesting, hybrid semiconductor NW-insulator-metal film structures are good candidates for plasmonic laser, or so-called SP amplification, by stimulated emission of radiation (spaser). As we know, the conventional dielectric laser size is limited above the half wavelength of the light in the dielectric materials, which is governed by diffraction law. However, SP breaks the limitation through storing the light into a deep subwavelength regime via collective oscillation of electrons. It means that the size of plasmonic lasers can be pushed down to tens of or even several nanometers, promising for the future ultra-small-size integrated electric and photonic chips in industry. Oulton et al. proposed and designed a semiconductor NWs-insulator-metal film system that

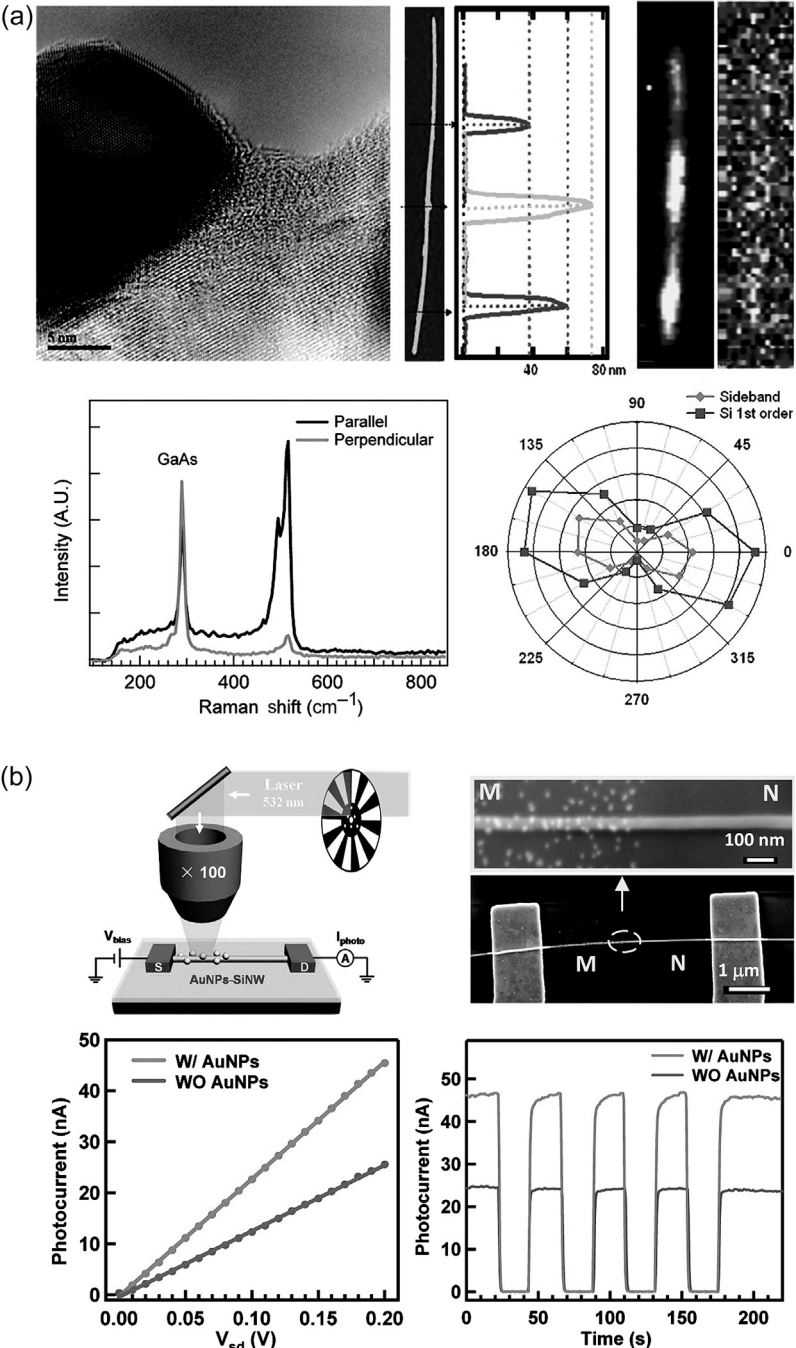


Figure 18.13 Surface plasmon-enhanced Raman and photocurrent of Si NWs. (a) Ag NPs are decorated onto Au surface via an epitaxial growth with surface reduction process (TEM image, upper left). The Raman mapping images show that the Raman intensity of the Si transverse

can generate plasmonic lasing (Oulton et al., 2009). As Figure 18.14(c) shows, the electromagnetic energy is extremely concentrated into the SiO₂ layer via SPP, which promises a high mode confinement and low propagating loss. In the other side, the CdS NW serves as high-gain material and the good facets naturally form a longitudinal SP cavity. When the CdS NW is below the diffraction limit ($\sim 50\text{--}120\text{ nm}$), strong visible lasing ($\sim 490\text{ nm}$) is achieved in this structure, demonstrating the achievement of plasmonic lasing (Figure 18.14(c)). At the same time, the emission output from the NW end exhibits polarization along the NW axis, while the emission of CdS NW supported on bare SiO₂ is polarized vertical to the NW axis, further confirming occurrence of plasmonic lasing (Oulton et al., 2009).

Very recently, more and more fascinating and novel phenomena mediated by SP have been observed in the semiconductor NWs near to metal structures. Cho et al. show the generation of hot-exciton emission is enhanced by the highly concentrated electromagnetic fields supported by the resonant whispering-gallery plasmonic nanocavities of CdS–SiO₂–Ag core–shell NW devices (Cho et al., 2011). The dominant hot-exciton emission during the exciton decay process greatly enhanced the radiative rate of excitons in CdS NWs, which is confirmed by a sharp decrease of CdS exciton lifetime from 1600 ns without Ag shell to 7 ps with Ag shell (Figure 18.15(a)). After that, the same research group demonstrated the first hot-luminescence emission of “bulk-sized” Si through coating the NW with a layer of Ag film, with the advantage of the intense localized electromagnetic field inside the semiconductor–insulator–metal hybrid structure (Figure 18.15(b); Cho et al., 2013).

18.3.2 Coupling between plasmon waveguide and photonic waveguide (electrical circuit)

Semiconductor photonic NWs exhibit low propagation losses, but the optical confinement is limited by the diffraction limit (Figure 18.16). Metal plasmonic NWs could manipulate light at the subwavelength nanoscale region, but suffering high propagation losses. The coupling and interconnection of photonic and plasmonic NW waveguides, forming photonic–plasmonic optical circuits, is an interesting strategy to realize all optical devices (Guo et al., 2009; Law et al., 2004; Pyayt, Wiley, Xia, Chen, & Dalton, 2008; Sirbully et al., 2005; Wu et al., 2013; Yan, Pausauskie et al., 2009).



optical (TO) phonon detected from the Ag NP–Si NW junction is 7-fold of the place without Ag NP (upper right). The TO Raman intensity at the Ag NP–Si NW when the excitation polarization is along the NW axis is 10 times stronger than vertical polarization (bottom left). Detailed polar plots of TO Raman intensity versus excitation polarization exhibits a 10°–15° distortion compared with previous works (bottom right) (Peng et al., 2010). (b) The photocurrent of single Si NW is increased by 100% by decorating the Au NPs (Chen et al., 2012). Adapted with permission from Peng et al. (2010), Chen et al. (2012). Copyright (2010 and 2012) American Chemical Society.

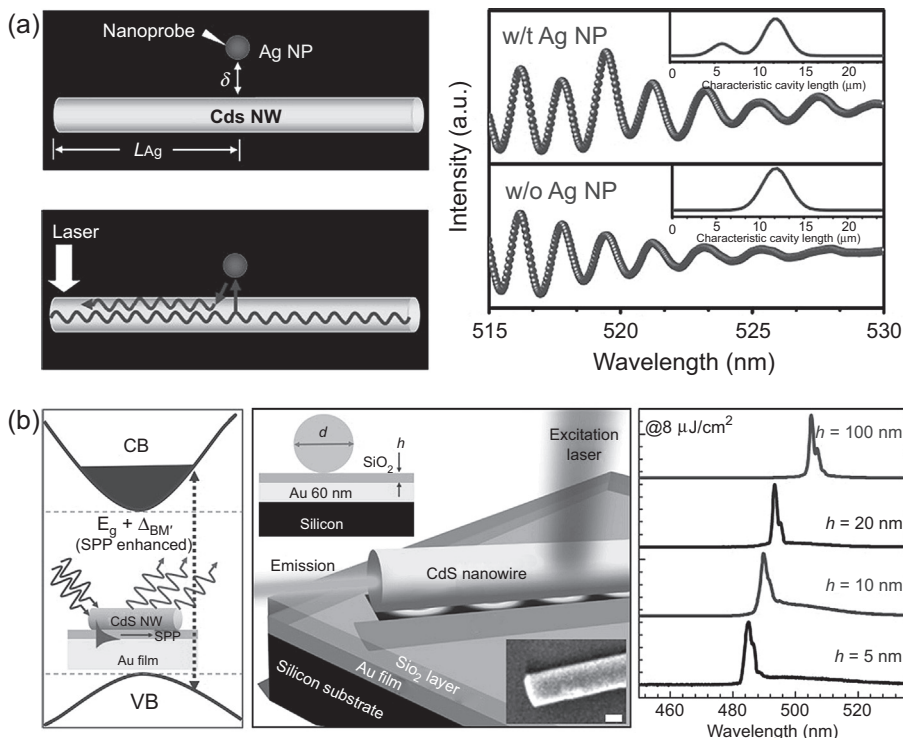


Figure 18.14 Localized surface plasmon and surface plasmon polariton-modulated cavity modes of semiconductor NW cavity. (a) Ag NP serves as a nanomirror that induces new F–P cavities. The Fourier transformations of photoluminescence F–P oscillations detected at the NW ends have one peak corresponding to the CdS NW cavity, while with Ag NP a new peak appears, and the frequency appears to be attributed to a cavity with length equal to the longitudinal distance between Ag NP and the NW end (Zhang et al., 2011). (b) The Burstein–Moss effect of CdS NW is greatly enhanced as well as the observation of strong Purcell effect with the presence of the localized electric field (left). The lasing wavelength dependent on the bandgap of CdS NW is blueshifted as a consequence (right). The localized field and exciton–surface plasmon interaction increases with the decrease of SiO₂ thickness, leading to a larger blueshift of the lasing wavelength (Liu et al., 2013). (c) Surface plasmon laser based on a semiconductor NW–insulator–metal film hybrid structure. The mode simulation shows that the electromagnetic field is extremely confined into a 5-nm-thick insulator layer via surface plasmon polariton, which in laser mode has areas as small as $\lambda^2/400$. In this structure, the CdS NW serves as gain media to overcompensate the Ohmic and radiation loss during the propagation of surface plasmon and provides a high-quality cavity. Even when the CdS NW diameter is as small as 50–120 nm, in which the photonic modes are prohibited, strong lasing is observed, confirming the achievement of plasmon nanolasers (Oulton et al., 2009).

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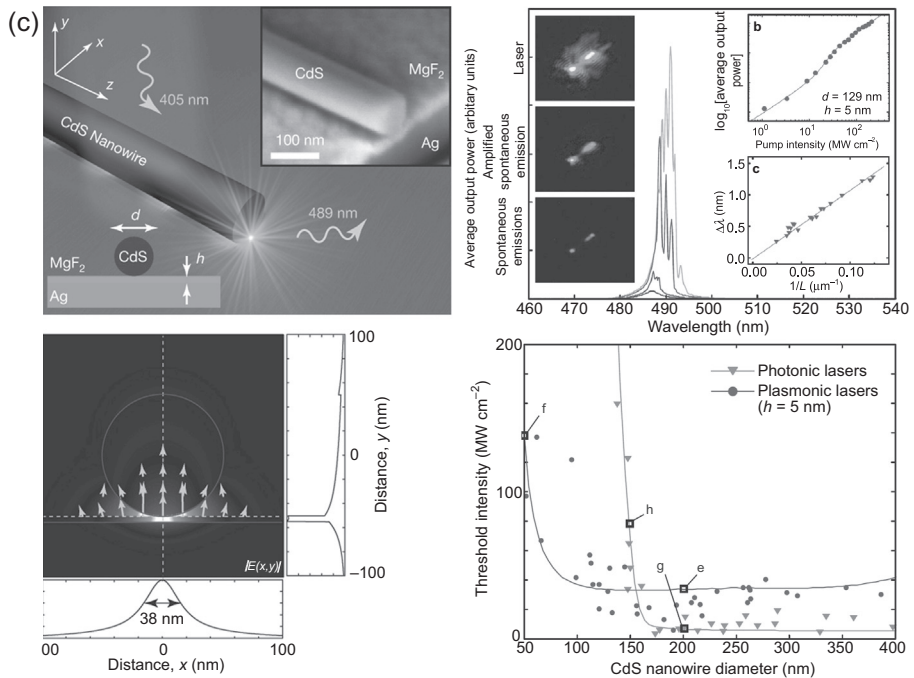


Figure 18.14 cont'd.

Yan et al. demonstrated a prototypical photonic–plasmonic routing device by directly coupling SnO₂ NW and Ag NW (Yan, Pausauskie et al., 2009). The PL of SnO₂ was excited by UV light, and emitted photons travel in the SnO₂ waveguide and scatter into Ag NW, exciting SP. The SPs propagate in Ag NW and then scatter into free space at the distal end of Ag NW. They found the coupling efficiency is determined by the coupling angle of two NWs. The end-emission spectra traveled through Ag NW redshift, due to the large propagation losses of high-frequency light. They use optical fiber to couple light into SnO₂ NW and measure the propagation length in Ag NW for different wavelength. The SnO₂–Ag–Ag devices and SnO₂–Ag–SnO₂ coupling devices were also exhibited.

Guo et al. demonstrated a similar idea by using Ag NWs and ZnO NWs (Guo et al., 2009). Through a tapered optical fiber, the light can be coupled into ZnO NW and then into plasmon in Ag NW. The opposite, exciting plasmon in Ag NW first and then converting to photonic modes in ZnO NW, can also be performed. The coupling efficiency between Ag NW and ZnO NW is dependent on light polarization. The Mach–Zehnder interferometer and hybrid microring cavity were also exhibited.

The electrical excitation and detection of plasmon is significant for densely integrated electronic–photonic devices (Figure 18.17). Falk et al. demonstrated a near-field electrical detection of optical plasmons (Falk et al., 2009). They used an Ag NW crossing a Ge NW field-effect transistor to detect plasmon. The Ag NWs guide SPs to the Ag–Ge junction. The plasmons are converted by the electron–hole pair and

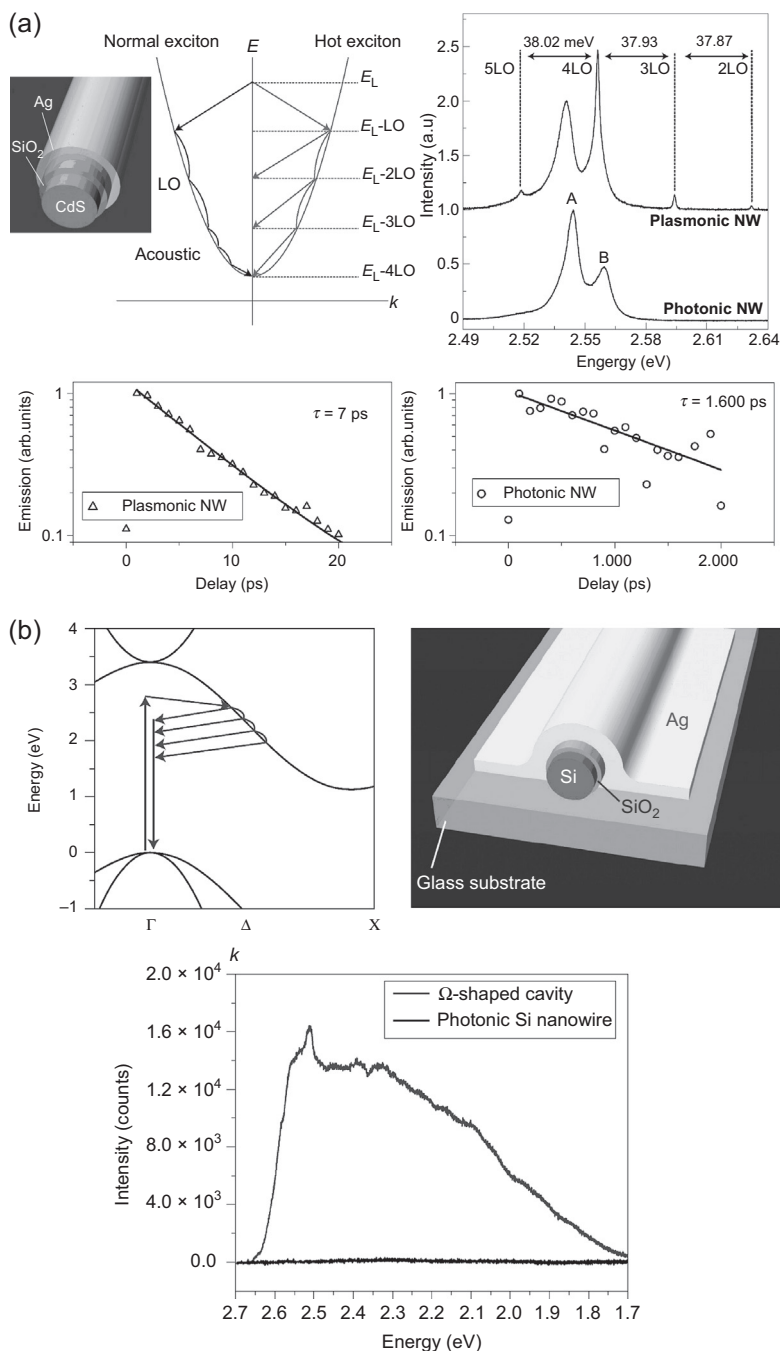


Figure 18.15 Hot-exciton emission and hot-luminescence emission mediated by surface plasmons. (a) In the core-shell CdS-SiO₂-Ag NWs, a strong localized electromagnetic field is induced in the resonant whispering-gallery plasmonic nanocavities. The non-thermalized hot-exciton emissions are greatly enhanced by the strong field and play a dominant role in the exciton decay channel, giving rising to an ultrashort exciton decay time (7 ps) (Cho et al., 2011). (b) In the Ω -shaped Si-SiO₂-Ag core-shell cavity, a phonon-assisted hot luminescence is observed before thermalization of the carriers to the minimum of the conduction band (Cho et al., 2013).

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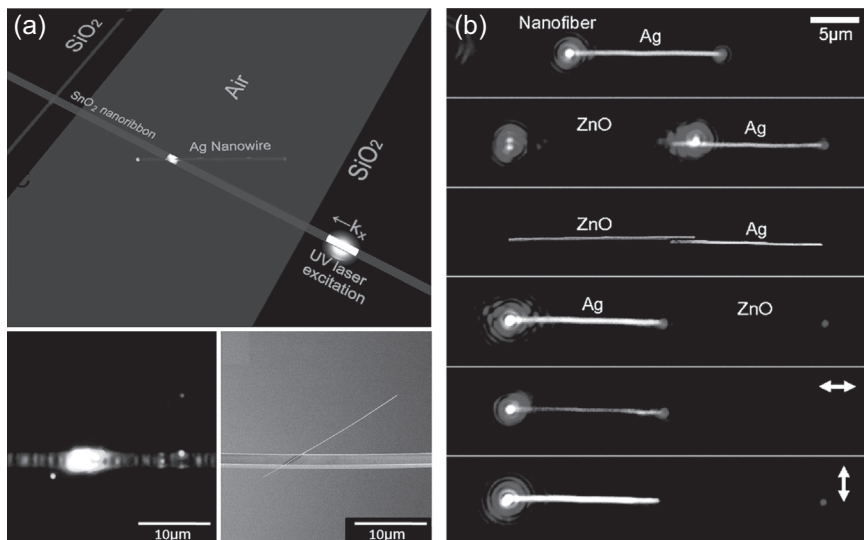


Figure 18.16 Coupling between plasmon waveguide and photonic waveguide. (a) Schematic representation (upper image) of the photonic–plasmonic routing device showing an Ag NW/SnO₂ nanoribbon cross-junction structure suspended between two SiO₂/Si wafers. A UV laser beam was focused on the right part of the SnO₂ nanoribbon to excite broadband PL. The PL is then waveguided along the nanoribbon to the metal–dielectric junction (the large bright spot shown in the actual optical microscope image at bottom left). Light scattered at the junction was coupled into surface plasmon modes of the Ag NW, which then propagated along the wire and finally scattered back into free space photon at the two distal ends (the two small bright spots) (Yan, Pausauskie et al., 2009). (b) Experimental observations of light coupling between silica nanofibers, ZnO NWs, and Ag NWs. Light from the nanofiber can excite plasmons in the Ag NW directly or via an intervening ZnO NW. Plasmons in the Ag NW can convert back to light in the ZnO NW. An SEM image show the diameter of the ZnO NW is 340 nm and the diameter of the Ag NW is 320 nm. The outputs of ZnO NW and Ag NW are polarization dependent (Guo et al., 2009).

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detected as current through Ge NW. The electrical plasmon detection could lead to detecting and imaging without far-field optical measurement. In cooperation with the electrically driven plasmon method, the plasmon circuit could be integrated into optoelectronic devices.

18.4 Summary

We have shown that metallic NWs can be applied as plasmonic waveguides and understood the excitation, propagation, and emission properties of plasmon. By setting

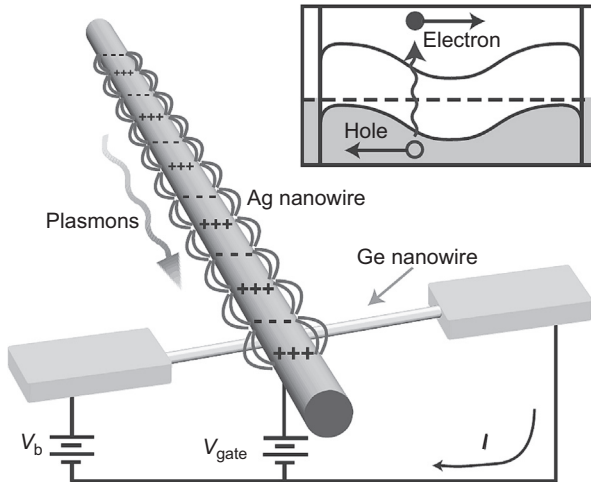


Figure 18.17 Electrical detection of plasmon in integrated electronic–photonic devices [Falk et al. \(2009\)](#). Schematic diagram illustrates the electrical plasmon detector operation. Besides the current of direct photo-response with laser focusing on the Ge NW, current is also recorded when the laser is focused at the two ends of Ag NW ($V_b = 0$, $V_{gate} = 0$). Inset: Electron–hole pair generation and separation in the Ge NW detector. Adapted with permission from [Falk et al. \(2009\)](#). Copyright (2009) Nature Publishing Group.

up plasmonic NW networks, more complex functions with signal transferring and information processing could be realized. The exciton–plasmon interaction in hybrid plasmonic/semiconductor NWs provides diverse and exciting properties and makes them show great potential for photonic devices and applications. The coupling between semiconductor waveguide and plasmonic waveguide can combine the advantages of both. Promising strategies for future electronic and photonic devices and applications can be expected.

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Electrical interfacing of nanowire devices with cells and tissues

19

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19.1 Introduction: interfacing to cellular systems

19.1.1 *Why do we build interfaces between nanoelectronic and cellular systems?*

Semiconductor science has become a driving force in the modern world as demand for more computing power and smaller devices has increased. This influence has provided more motivation for developing control of nanoscale device fabrication and synthesis (Comm. Technol., Subcomm. Nano. Sci. Eng and Technol., 2010; Jeong, Doris, Kedzierski, Rim, & Yang, 2004; Lieber, 2011; Lu & Lieber, 2006, 2007; Lu, Xie, & Lieber, 2008). This has led to a multitude of new nanomaterials such as graphene, nanoparticles, and nanowires (NWs), which can then have their geometries, organization, and physical properties designed and controlled on the nanoscale (Jeong et al., 2004; Lu & Lieber, 2007; Cui & Lieber, 2001; Duan, Huang, Cui, Wang, & Lieber, 2001; Friedman, McAlpine, Rickette, Ham, & Lieber, 2005; Rogers, Lagally, & Nuzzo, 2011; Sun & Rogers, 2007; Yan et al., 2011).

Semiconducting NWs have several desirable traits for use in interfacing with biological systems. NW structure can be designed de novo, allowing for multifaceted yet precise modulations in NW defects (Algra et al., 2008; Caroff et al., 2009; Tian et al., 2007), doping (Li, Qian, Xiang, & Lieber, 2006; Yang, Zhong, & Lieber, 2005), composition (Duan et al., 2001; Li et al., 2006; Bjork et al., 2002; Gudiksen, Lauhon, Wang, Smith, & Lieber, 2002; Yang et al., 2005; Jiang et al., 2011; Lauhon, Gudiksen, Wang, & Lieber, 2002; Dick et al., 2004), and topography (Schwarz, Tersoff, Kodambaka, Chou, & Ross, 2011; Tian et al., 2010; Tian, Xie, Kempa, Bell, & Liber, 2009). This high degree of control enables researchers to create NW units with predictable properties for use as building blocks for multicomponent materials, which can explore the inorganic/biology interface. Finally, the tunable electrical properties of semiconducting NWs allow for the exploration and potential control of the bioelectric properties of cells.

“Mesoscale” is the natural length scale for electrical interfaces with cellular components.

Communication and signaling in biological systems, ranging from single cells to tissues, occur primarily through discrete and organized mesoscale structures (ranging from a few nanometers to one micron), such as proteins and their self-assembled structures. The mesoscale thus represents the natural length scale on which to focus in order

to build device interfaces that actively deliver input and output (I/O) signals to cells and cellular assemblies. Such mesoscale interfaces not only will enable high-efficiency signaling to and from biological mesostructures, but may ultimately blur the distinction between natural and artificial interfaces, leading to breakthroughs in biological science and engineering (Patolsky, Timko, Zheng, & Lieber, 2007; Timko, Cohen-Karni, Qing, Tian, & Lieber, 2010). Explorations using semiconducting NWs in cellular systems give researchers the potential to observe such mesoscale interactions with unprecedented detail. Additionally, such interactions can be utilized to gain knowledge applicable to human health by stimulating, making recordings of, and delivering objects to single cells and tissues in a controlled manner while minimizing detrimental effects (Patolsky et al., 2007; Timko et al., 2010).

19.1.1.1 Two platforms for NW-based cellular studies

NW based platforms in the biomedical sciences can be divided into two categories: *basic platforms*, which can address current life science questions, and *advanced platforms*, which are designed to test previously unexplored interactions or biophysical properties of cellular components. First, applications of the basic NW systems use conventional NW materials to create a device with well-known physical and chemical properties. These devices are easier to create and have been around for longer, and they have been utilized in a wide range of nonbiological applications such as energy scavenging systems (Boettcher et al., 2010; Fan, Razavi, et al., 2009; Garnett & Yang, 2010; Kelzenberg et al., 2010; Qin, Wang, & Wang, 2008; Wang & Song, 2006; Wang, Song, Liu, & Wang, 2007; Xu et al., 2010) and components for integrated circuits (Fan, Ho, Jacobson, Razavi, & Javey, 2009; Fan, Ho, Takahashi, et al., 2009). Biomedical researchers have adopted *basic platforms* such as planar NW field-effect transistors (FETs) (Fan, Ho, Jacobson, et al., 2009; Javey, Nam, Friedman, Yan, & Lieber, 2007; Nam, Xiang, Xiong, Ham, & Lieber, 2009; Whang, Jin, & Lieber, 2003) and vertical NW arrays (Boettcher et al., 2010; Garnett & Yang, 2010; Kelzenberg et al., 2010; Qin et al., 2008; Wang et al., 2007; Wang & Song, 2006) for biomolecular sensing (Patolsky et al., 2007; Timko et al., 2010), extracellular recording (Patolsky et al., 2007; Timko et al., 2010), drug delivery (Chevrier et al., 2011; Kim, Ng, Kunitake, Conklin, & Yang, 2007; Shalek et al., 2010), and localized cellular imaging (Xie, Hanson, Cui, & Cui, 2011). Recent progress in nano- and micro-fabrication has stimulated rapid development in *advanced platforms*, conforming them to the specific demands of biology and medical science. Examples of these platforms include intracellular FET probes (Duan et al., 2012; Gao et al., 2012; Jiang, Qing, Xie, Gao, & Lieber, 2012; Tian et al., 2010) and nanoelectronic innervated synthetic tissues (Tian et al., 2012), both of which will be covered further in this chapter.

19.1.2 Why do we need semiconductors?

19.1.2.1 Semiconductors yield higher sensitivity

Semiconductor NWs' detection range, through converting small deviations in molarity to electrical signals, can span many orders of magnitude, down to femto-molar

sensitivities (parts per quadrillion) (Li et al., 2013; Zheng, Patolsky, Cui, Wang, & Lieber, 2005). Similar analytical techniques such as inductively coupled plasma mass spectrometry can, with specialized methods, report similar detection limits, but they irreversibly destroy the samples. NW field-effect transistors (NWFETs) can operate innocuously in physiological conditions, allowing for highly sensitive probes of cellular system. This unique ability of NW sensors suggests great potential in the study of non-equilibrium behavior of cells. Beyond chemical transduction, semiconducting NWs have been utilized for recording intracellular electrochemical potentials (Kim et al., 2007; Qing et al., 2010; Tian & Lieber, 2013).

In 1963, the Nobel Prize in physiology and medicine for the discovery of the ionic mechanism of action potential formation in neurons brought the study of electrochemical potentials in cells to the fore. Almost 30 years later, Sakmann and Neher were awarded the Nobel Prize in 1991 for advancing the field with the patch clamp technique. When using the patch clamp technique, a pulled glass micropipette of about 1 μm is filled with electrolyte and sealed to a patch of the membrane of a cell. Through the electrolyte in the pipette, intracellular electrical measurements with a high signal-to-noise ratio (S/N) and single ion channel recordings are possible (Sakmann & Neher, 1984). However, if the probes decrease in size, the S/N decreases because the tip's impedance is inversely proportional to the pore size. This can lead to increased clogging and large noise levels at submicron scales (Zhao et al., 2008). Semiconducting NWFETs offer a potential solution to this problem, as they utilize a different mechanism that is not inversely proportion to size.

19.1.2.2 Semiconductors yield smaller, less invasive devices

As mentioned above, microelectrode devices are intrinsically limited by impedance issues at the nanoscale, with 50 and 500 nm being the lower limits for glass and carbon nanoelectrodes (Tian & Lieber, 2013). As seen in Table 19.1, in contrast to microelectrodes, NWFETs are only limited by the techniques for their synthesis and fabrication, yielding a lower bound of tip sizes of 5–10 nm. Additionally, it is possible to place multiple sensors within a region of space, leading to increased spatial resolution. The small sizes of the active parts in NWFETs also decrease the mechanical invasiveness of this technique.

An additional drawback of microelectrode devices is that their passive circuit design makes them more electrochemically invasive. Microelectrode techniques pass ions and currents through the cell, which means the cell can experience deleterious effects of modulations of voltages or current that could interfere with natural processes. NWFET techniques use the cell to externally modulate the NW conductance (see Section 19.2). There is no exchange between the cytosol and NW, making the technique less invasive. Injecting foreign electrolytes and disrupting the membranes of cells by around a micron (eukaryotic cells are tens of microns while prokaryotic cells are 1–5 microns) results in a highly invasive technique, making it hard to maintain natural cell behavior. NWFETs are much smaller in scale and introduce no foreign electrolytes. The invasiveness of NW probes can be further reduced by modifying the

Table 19.1 Comparison of traditional micropipette techniques and a NanoFET

IC technique	Equivalent circuit	Size (nm)	Calibrations	Capabilities	Invasiveness	Cellular entrance
Glass micropipette (b,d)		~50–5000 impedance limited	Both amplitude and shape	Can record both current and voltage Single ion channel to whole-cell recording	Electrochemical and mechanical	Mechanical or electrical
Carbon or metal micro-/nanoelectrode (c)		~500–1000 impedance limited	Both amplitude and shape	Can record both current and voltage Whole-cell recording	Electrochemical and mechanical	Mechanical or electrical
NanoFET (a)		~10–100	Amplitude	Can record only voltage Whole-cell recording Multiplexing is scalable High spatiotemporal resolution	Minimal	Biological

Adapted with permission from [Tian and Lieber \(2013\)](#).

surface of the NW with an artificial phospholipid bilayer, which allows for integration of the NW with the cellular membrane by membrane fusion.

19.2 Signal transduction mechanism: field-effect transistor-based detection

19.2.1 Basic principles and schematics

All of the detection methods mentioned in the first section are based on the concept of FETs. The FET was first made in 1926 by Julius Edgar Lillienfeld, but it was not until 1952 that William Shockley at Bell Labs fully explained its function (Shockley, 1952). The FET is a voltage-controlled resistor. It consists of a source, drain, and gating potential. Current comes out of the source, and flows through the gating voltage, which modifies the internal conductance, which in turn modifies the current, which then flows out the drain. FETs were first applied as chemical signal transducers over three decades ago, and have been thoroughly reviewed (Domansky, Janata, Josowicz, & Petelenz, 1993; Janata, 1994). Historically, these devices have been difficult to maintain and have had low chemical sensitivity. To rectify these problems, the Lieber group created FETs using controlled Si NW doping in 2000 (Cui, Duan, Hu, & Lieber, 2000). Unlike planar predecessors, these NWFETs are on the same length scales as biomolecules and other cellular components, giving rise to ultra-sensitive electrical detection.

NWFETs detect chemicals and potential variations by modulating the internal current that is sent through the wire. NWFETs use a semiconducting NW as the channel component. An example is n-doped silicon with metal ohmic contacts at both ends, which act as source and drain electrodes that allow current to flow through the wire (Figure 19.1). The conductance of the NW is sensitive to applied electric fields and

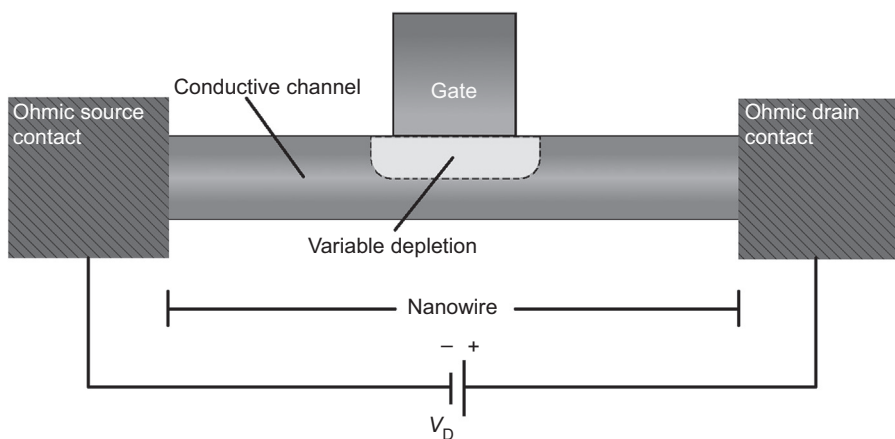


Figure 19.1 NWFET schematic. Metal source and drain contacts are connected to a central NW channel. The potential difference between the source and drain allows current to flow through the conductive channel. Current is then modulated by the gating electrode.

surface charges, as they will change the number of charge carriers available in the silicon. The current passing through the wire is then modulated by these changes in conductance, as the fields around the NW act as the gating element capacitively coupled to the system via the dielectrics. In the specific case of n-doped NWs, a negative gating voltage reduces the number of mobile charge carriers, reducing the conductance. Applying a positive voltage has the opposite effects. The conductance can be readily monitored, which allows the NW surface to act as a sensor for endogenous electric signals from the biological systems.

19.2.2 Short-channel device towards localized sensing and enhanced sensitivity

Dopant modulation can be used to limit the size of the channel length in an NWFET. This reduction in channel size can yield finer spatial resolution, enhance sensitivity, and decreased switching speed. With a small region accepting a gate voltage, the bioelectric behaviors of fewer and fewer molecules can be detected electrically. For example, this technique could one day be used to probe individual cellular component such as ion channels or organelles.

In order to turn the NW into an FET, most of the NW must be effectively inert to conductance changes, and a small highly responsive region forms the sensitive channel. This is commonly accomplished by using heavy doping such as n^{++} or p^{++} doping to make most of the wire highly conductive, and then using light n^- or p^- doping to make a small region slightly conductive to serve as the sensitive channel (Figure 19.2(b)) (Cohen-Karni et al., 2012). Additionally, as Jiang et al. explored (2011), sensors can also be created with a p/n diode configuration, as seen in Figure 19.2(c) (Cohen-Karni et al., 2012). Typically, applications of these diode-based NWs involve photovoltaics, but the depletion region can also serve as a sensing component.

Using these doping schemes, devices can be created using different fabrications to optimize their sensitivity. While the NWs are being grown, pressure inside the CVD chamber can be modulated to cause kinks in the growth (Tian et al., 2010). The results can be used to create a device that can act as a probe (Figure 19.3). The kinked wire is patterned on a sacrificial layer, which allows it to be flexible and three dimensional. This technique and its applications are further discussed in Section 19.4.2.

19.3 Nanowire sensors for extracellular electrical recording

Biological systems are organized as hierarchical networks operating on spatial and temporal scales. At all of these scales — from the single organelle to the entire body — electric fields play an important role. For example, without the potential present across most membranes, aerobic respiration would be impossible. Unfortunately, the use of metal electrodes for probing these systems is inherently limited, as impedance

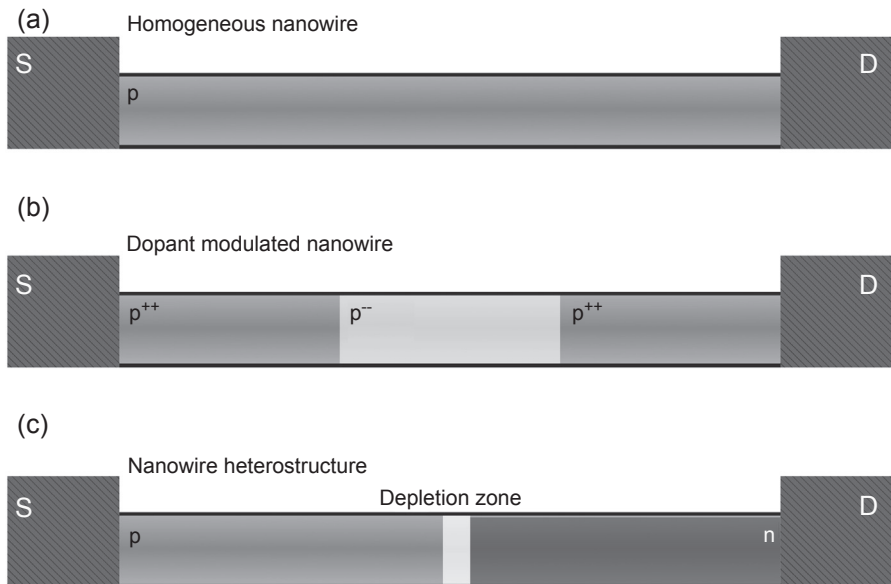


Figure 19.2 Short channel length schematic. (a) In the case of a uniformly doped NW, the entire region is an active FET. (b) The lightly doped central region is most sensitive to gating voltages, decreasing the size of the sensor. (c) In p–n NWs, a small depletion region forms at the interface between the doped regions, limiting the sensor size.

increases as the electrodes get smaller, meaning that sufficient spatial resolution cannot be obtained (Cui & Lieber, 2001; Duan et al., 2001). As detailed in the above sections, NWFETs offer a solution to the limitations of older microelectrodes, and some of their applications are explored in the next sections.

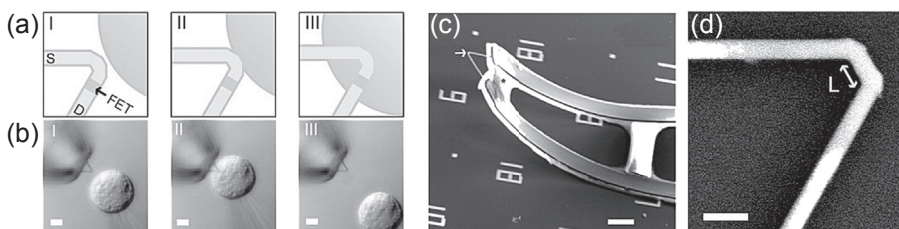


Figure 19.3 Kinked NW bioprobe. (a) Diagram depicting the NW internalization process. (b) The NW first approaches the cell surface (I), then contacts and enters the cytoplasm of the cell (II). Finally, the probe is retracted after experimentation (III) (scale bars 5 μm). (c) Scanning electron micrograph of the device (scale bar 5 μm). (d) Zoomed in SEM view of the tip, revealing the kinked structure of the NW (scale bar 200 nm). Adapted from Tian et al. (2010), with permission.

19.3.1 Extracellular electrical recordings

NWFETs can be created to interface with the extracellular matrix as point-like probes. The channel width can be restricted to such a small region that NWFETs can measure single ion channels or groups of ion channels (Figure 19.4(a)). These NWFETs can also be multiplexed to measure signal transduction speeds in the membrane (Patolsky, Timiko, Yu, & Fang, 2006).

Cohen-Karni et al. in 2012 were able to monitor cellular beating in embryonic chicken cardiomyocytes (Cohen-Karni et al., 2012). Figure 19.4 shows the recordings taken by several NWFETs in different locations showing a regular beating pattern across the cell network. By correlating the placement of these NWFETs, Cohen-Karni et al. were able to study the propagation of the signal. At short distance, $\sim 1.9 \mu\text{m}$, a speed of $\sim 0.17 \text{ m/s}$ was recorded; while at longer distances, $\sim 73 \mu\text{m}$, a speed of $\sim 0.35 \text{ m/s}$ was recorded. Older systems, such as high-density microelectrode arrays, are unable to perform such measurements, as the electrodes are still electrically correlated at this length scale, meaning that the movement of the signal cannot be resolved. Better understanding of these signals is important in the evolving studies of cellular signaling dynamics.

19.3.2 Electrical recordings from synthetic tissues

The majority of systems that have been studied *in vitro* have been 2D, which is problematic, as real biological systems are 3D. NWFETs are small enough to be combined with synthetic 3D biomaterials to monitor 3D tissues (Tian et al.,

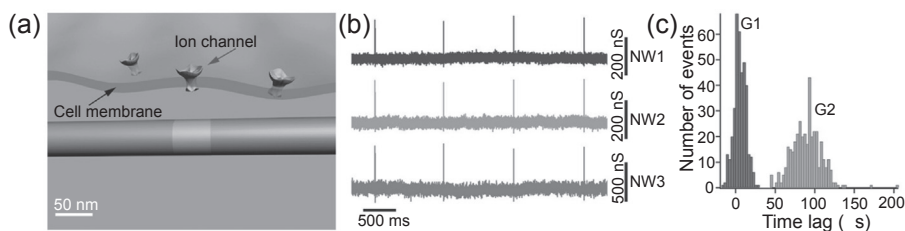


Figure 19.4 NWFET extracellular use. (a) Schematic illustrating NWFET measuring the potential of transmembrane ion channels. (b) Representative data from several correlated NWs measuring a localized group of cardiomyocytes. (c) Time-resolved data indicating a time lag between two groups of signaling cardiomyocytes. G1 shows the time delayed data when the two NW sensors are $1.9 \mu\text{m}$ apart. G2 shows the time delay data when the two NW sensors are $73 \mu\text{m}$ apart. These data allow for signaling speeds to be calculated.

Adapted from Cohen-Karni et al. (2012), with permission.

2012). A single NWFET can monitor a single ion channel, while a network of NWFETs can monitor a whole tissue sample or even organ (Figure 19.5). 3D bio-materials offer a better method for connecting the results from 2D cell cultures and *in vivo* studies than current strategies. Coupling electronics to this new system can look into the pharmacological response of cells in 3D (Tian & Lieber, 2013). NWFETs can be integrated into this biological system better than current planar electrodes, because they are smaller, cause less damage, and have better spatial–temporal resolution.

In 2012, Tian et al. accomplished this by synthesizing kinked or uniform silicon NWs (Figure 19.6). After registering their position and electrically connecting them, they were arranged and integrated into a freestanding macroporous scaffold, which is referred to as a nanoelectronic scaffold (nanoES). Cells were then cultured within the nanoES (Tian et al., 2012). To showcase the platform’s potential uses, norepinephrine — a hormone and neurotransmitter that is used as a low blood pressure medication — was introduced into a 3D scaffold with cardiac cells. NWFETs recorded an increase in pulses, which are seen as changes in conductance by the NWFETs, and this result suggests that continuous electrical monitoring can be used for *in vitro* drug studies.

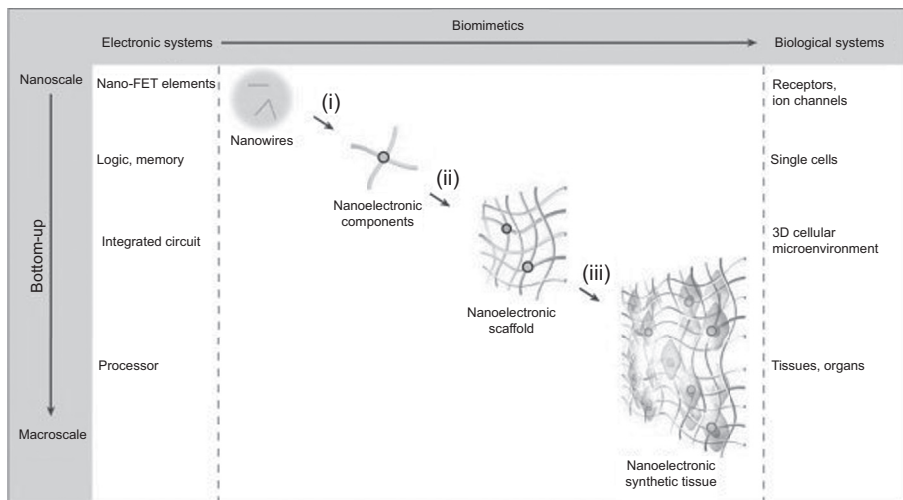


Figure 19.5 Integration of nanoelectronics with cells and tissue. Integrated biological and nanoelectronics can be created with discrete electronic and biological components. The steps to assemble these integrated systems are biomimetic. (i) NWs are patterned into FETs. (ii) 3D NWFETs/nanoES are assembled with traditional extracellular matrices. (iii) Incorporation of cells and growth of synthetic tissue through biologic processes. Adapted from Tian and Lieber (2013), with permission.

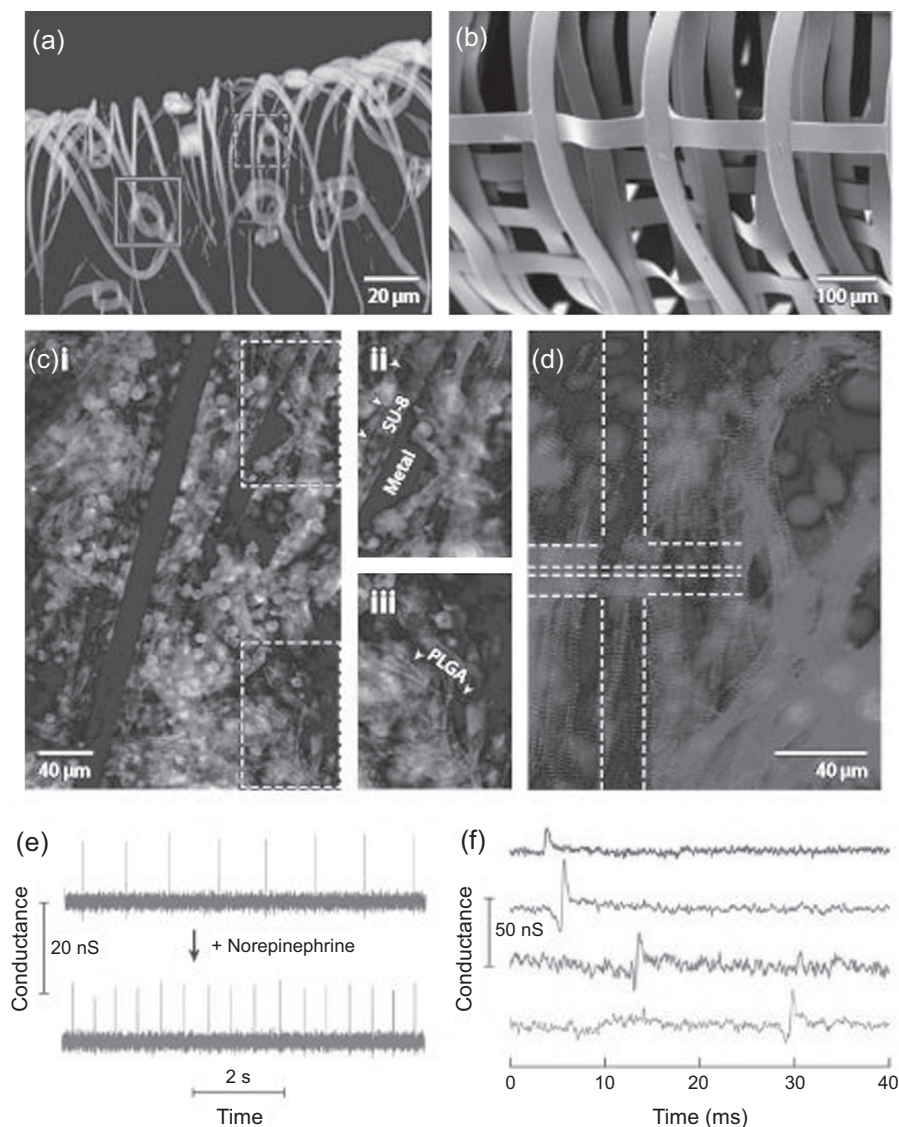


Figure 19.6 NanoES and synthetic tissues. (a) 3D reconstructed confocal fluorescence micrographs of reticular nanoES. The scaffold was labeled with rhodamine 6G. The two outlined squares indicate different FETs present in the nanoES. (b) Scanning electron microscope image of a mesh nanoES. (c) (i) Confocal fluorescence micrograph of cardiac patch grown on ES. (ii, iii) Zoomed-in views showing metal interconnections, the scaffold (labeled SU-8), and electron spun poly(lactic-co-glycolic acid) fibers. (d) Epifluorescence of the surface of the cardiac patch with labeled actin and cell nuclei. The position of the source and drain electrodes are represented by dashed lines. (e) Conductance versus time recorded by a single NWFET before and after introduction of norepinephrine. (f) Multiplex electrical recording of extracellular field potentials from four different NWFETs in the mesh nanoES. Data traces for a single spike recorded at each different NWFET.

Adapted from [Tian and Lieber \(2013\)](#), with permission.

19.4 Nanowire sensors for intracellular electrical recordings

19.4.1 *The importance of intracellular recordings and the advantage of nanowires*

Recent research has emphasized the important role that bioelectrical communication plays in the growth and organization of biological systems (Levin & Stevenson, 2012). The cell membrane creates a separation of charged particles, which results in an electrical voltage potential across the membrane. It has been found that different cell types have different resting membrane potentials: more mature, terminally differentiated cells tend to be hyperpolarized, and more plastic, rapidly proliferating cells tend to be depolarized (Binggeli & Weinstein, 1986). This is more than a passive byproduct of other pathways, as artificial depolarization and hyperpolarization can respectively induce and inhibit cell proliferation, and they have the opposite effect on stem cell differentiation. In addition to creating an ion gradient, cell membranes have resistance and capacitance, which results in intracellular signals being distorted when read by extracellular detectors (Tian & Lieber, 2013). Even though many cell-signaling pathways begin when extracellular signaling molecules interact with their target cell-surface receptor, it is the ensuing intracellular interpretation of that signal that results in cellular action. Clearly it is of great importance to have devices that are able to record and interpret such intracellular signaling.

Although non-NW means of making intracellular recordings currently exist, these methods all have drawbacks and limitations (Tian & Lieber, 2013). Voltage-sensitive optical dyes and proteins can make intracellular recordings with high spatial resolution (Kauer & White, 2001), but have a limited S/N, issues with biotoxicity, and trouble differentiating signal spikes (Grinvald & Hildesheim, 2004). Single-terminal glass or carbon microelectrodes are capable of mechanical insertion into cells, but such electrical probes require direct ionic or electrical junctions between the probe tip and the cytosol (Ewing, Strein, & Lau, 1992). This is problematic, as it must be small enough to enter the cell without damaging it, but large enough that the junction impedance is low to the point where thermal noise and cellular signals can be differentiated. Finally, such devices are not well suited for communicating with other electronics, which makes them poor choices for cell-machine communication.

NWs, particularly in the form of NWFETs, are well suited for making probes for intracellular recordings (Tian & Lieber, 2013). Such devices can be as small as 10 nm, which allows them to enter the cell noninvasively, even using the cell's natural endocytic pathways (Nel et al., 2009). NWFETs can interface with cells without the need for a direct exchange with ions, and can detect cellular potential and biological macromolecules. Finally, it is possible to integrate multiple FET active channels into one device during the synthesis process, which makes these devices apt for making multiplexed intracellular recordings.

19.4.2 Kinked nanowire field-effect transistors

19.4.2.1 The first FET for intracellular electrical recording

The largest issue with creating an intracellular NWFET is that a traditional FET is planar and rigid. Traditionally, the active channel is linearly connected to the source and drain, which are too large to be noninvasively inserted into a cell (Lu & Lieber, 2007). A solution to this problem was first developed by Tian, et al. (2010); the active channel is a kinked NW and the arms serve as the source and drain (Figure 19.7 and Figure 19.11). The arms are connected to metal interconnects, which bend the kinked tip upwards, enabling the active channel of the FET to enter the cell without the bulky metal electrodes interfering with the cell.

Tian et al. (2009) had previously determined that changes in reactant pressure during SiNW growth could create reproducible 120° cis-kinks, and the junctions could be controllably doped. This process was used to form the probe tip. Two cis-linked units were incorporated to create a V-shaped tip angle of 60° , and *in situ* doping during synthesis was used to localize the FET element adjacent to the geometrically defined tip. The spacing between the two legs was roughly 50 nm and the heavily doped FET element was about 200 nm long. Remote electrical interconnects to the S/D NW arms were created on an SU-8 polymer on top of sacrificial Poly(methyl methacrylate) (PMMA) layer. The probe was bent upwards and the PMMA layer removed, furnishing a stable, freestanding 3D FET (Figure 19.8). This was coated with phospholipid bilayers, enabling the device to fuse to cell membranes and function as an intracellular electrical probe.

The 3D NWFET probes were able to obtain a sensitivity of 4 to $8\ \mu\text{S/V}$ when measuring conductance versus a reference potential, which is the same as planar FETs, meaning the kinked geometry did not result in any loss of functionality (Tian et al., 2010). Moreover, its performance was not diminished by repeated

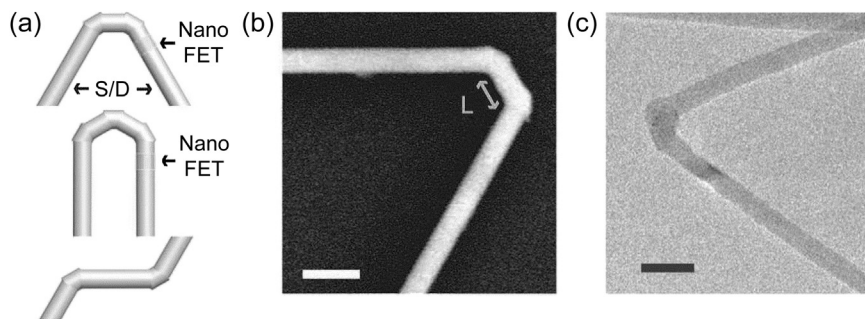


Figure 19.7 Synthesis of kinked SiNW probes. (a) Schematics of 60° (top) and 0° (middle) multiple-kinked nanowires and cis (top) and trans (bottom) configurations in nanowire structures. (b) SEM image of a doubly kinked nanowire with a cis configuration. L is the length of the segment between two adjacent kinks. (c) Transmission electron microscopy image of an ultrathin 60° kinked nanowire (scale bars: 200 nm (b); 50 nm (c)). Adapted from Tian et al. (2010), with permission.

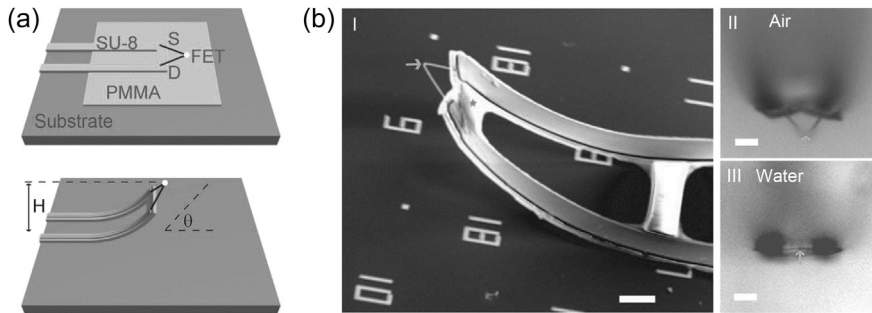


Figure 19.8 3D kinked nanowire probes. (a) Schematics of device fabrication. Patterned poly(methylmethacrylate) and SU-8 microribbons serve as a sacrificial layer and flexible device support, respectively. The dimensions of the lightly doped n-type silicon segment (white dots) are ~ 80 by 80 by 200 nm^3 . H and q are the tip height and orientation, respectively, and S and D designate the built-in source and drain connections to the nanoscale FET. (b) SEM (I) and bright-field optical microscopy (II, III) images of an as-made device. The arrow and star mark the nanoscale FET and SU-8, respectively. II and III are recorded in air and water, respectively (scale bars, $5 \mu\text{m}$).

Adapted from [Tian et al. \(2010\)](#), with permission.

bending, and its ability to function at different angles is important for interfacing with biological systems. This capacity was demonstrated by using the change in potential charge of the NWFET probe when it was inserted into a cardiac muscle cell to record the cell's intracellular potential. Within 250 ms of the probe being inserted into the cell, the recorded potential dropped to -52 mV , and then rose to and remained at about -46 mV until quickly returning to baseline upon being removed from the cell.

When placed in contact with spontaneously firing embryonic chicken cardiomyocytes, the 3D NWFET recorded conductance-versus-time data, which initially showed that the recordings being made were consistent with beating cardiomyocyte extracellular recordings. After less than a minute during which no external force was applied, a transition to a steady-state occurred. The initial extracellular recordings disappeared, and recordings depicting the characteristic five phases of cardiac intracellular action potential appeared. These results definitively show that the 3D NWFET as designed is capable of making intracellular recordings of biological systems.

19.4.2.2 Kinked NW diode for intracellular electrical recording

Another nanoscale probe has been developed using a kinked NW as a p–n diode ([Jiang et al., 2012](#)). The kinked NW was synthesized in a manner similar to the previously described device, except one leg was p-doped using boron and the other was n-doped using phosphine, localizing the active device element at the depletion region at the joint of the NW. In this device, the concentration of p-dopant was roughly 10 times lower than that of the n-dopant, causing the device to behave like a p-type FET.

The kinked p–n junction NW probe was successfully converted into a 3D probe capable of making precise intracellular recordings using a methodology similar to that of the original kinked 3D NWFET. After functionalization with a phospholipid bilayer, the device was able to make intracellular electrical recordings of spontaneously beating chicken cardiomyocytes that were consistent with the results obtained via patch clamp.

Although the current version of the probe is unable to do so, it is possible that the highly localized nature of the probe could enable detailed recordings of the potential distribution with cells and subcellular structures. Moreover, the device's current length of the p-depletion region, which defines the device's spatial resolution, is 210 nm; this means that the device can be further improved, as this is substantially worse than the theoretical limit of 10–30 nm. Finally, this design approach has a lot of potential, as altering the doping can make a p-type, n-type, or ambipolar FET, and it could possibly be turned into a 3D nanoscale photodetector.

19.4.2.3 Multiply kinked NWFETs for intracellular recording

This general design of using kinked NWs to produce NWFETs has been expanded to create more complex intracellular biological probes (Xu et al., 2013). By incorporating three instead of two cis-kinks, a U-shaped kinked NW was created that was turned into an NWFET using the same process as before. The U-shape enables the device to penetrate deep into cells and other materials without increasing the cross-sectional area. An improvement to the original V-shaped device was made by turning it into a multiplexed nanoFET detector. One way this was accomplished was by using controlled doping to put multiple FETs along the same arm of the kinked NW. Another route involved creating a W-shaped kinked NW (effectively two V-shaped kinked NWs grown continuously to form one W-shaped wire) and placing a nanoFET near both tips. Both designs allow for series and parallel multiplexing of intracellular signals, as well as simultaneous intracellular and extracellular recordings using a single probe.

19.4.3 Branched nanotube–nanowire field-effect transistor

19.4.3.1 Device design and fabrication

Although the kinked nanoFET was the first intracellular semiconductor device of its kind, the device design puts limitations on the probe size and its ability for multiplexing (Tian & Lieber, 2013). Such limitations encouraged the development of a device to overcome these limitations, and one such device is a branched intracellular nanotube FET (BIT-FET) (Figure 19.9) (Duan et al., 2012). An electrically insulating SiO₂ nanotube is integrated on top of an NWFET such as a SiNW. Once the tube penetrates the cell membrane, the cytosol fills the tube and comes in contact with the underlying FET, allowing for measurements of the intracellular transmembrane potential or action potentials.

The synthesis of a BIT-FET was accomplished by growing sacrificial germanium nanotubes on top of SiNWs via a gold-nanocluster-catalyzed vapor–liquid–solid

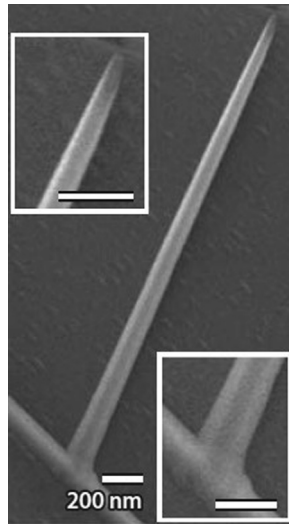


Figure 19.9 SEM image of a final nanotube on a silicon nanowire. Insets: magnified images of the top and bottom of the nanotube (scale bars: 200 nm).

Adapted from [Duan et al. \(2012\)](#), with permission.

(VLS) mechanism. On select branches, source and drain contacts were formed by electron beam lithography (EPL) and metal evaporation, and then the nanotube wall was formed by a controlled atomic layer deposition of SiO_2 . An initial etching with buffered hydrofluoric acid removed the top of the SiO_2 shell, exposing the germanium core, and an H_2O_2 etch removed the germanium, leaving the completed device behind.

19.4.3.2 Device capabilities

The BIT-FET was confirmed to have the capacity to be a functional intracellular recorder by showing that its sensitivity, measured as conductance as a function of water-gate-voltage, significantly improved after the germanium core was removed by etching (-170 nS/V vs -4530 nS/V) ([Duan et al., 2012](#)). This and other controls showed that the BIT-FET was responding with high selectivity to the solution inside the nanotube rather than outside of it. Furthermore, its bandwidth was measured to be greater than 6 kHz, which is sufficient for recording neuronal action potentials, and its small size makes it well suited for probing structures that are difficult to study through traditional means such as dendritic spines.

In a proof of concept test, the BIT-FET was used to record the intracellular potential of spontaneously beating embryonic chicken cardiomyocyte cells. The device was modified with phospholipid bilayers to promote nanotube internalization, and brought into contact with the cells. A recording of voltage versus time at first showed extracellular signals, but after approximately 45 s, a sudden transition to intracellular recordings was observed, generating a graph with the five characteristic phases of cardiomyocyte intracellular action potentials.

The fact that no force was needed to cause transition for extracellular to intracellular recording indicates that the nanotube is spontaneously penetrating the cell, possibly by lipid fusion. This is advantageous, as it forms a tight seal that prevents probe–membrane leakage, allowing for full-amplitude recording without the need for any correctional circuitry. Also, spontaneous penetration can occur for a wide range of orientations, making it easier for the nanoprobe to contact the cells. Finally, the tight seal coupled with the small size of the nanotube is expected to preserve cell vitality during the recording process, as well as facilitate multiplexed recordings from a single cell and cell networks, as multiple devices can simultaneously be making measurements of the same cell. There are, however, still limitations; the S/N is lower than traditional glass micropipettes and the devices are not currently able to stimulate the cells.

19.4.4 Active silicon nanotube transistor

19.4.4.1 Device design and fabrication

Another type of intracellular FET probe has been developed. It is a single conducting nanotube known as an active nanotube transistor (ANTT) (Figures 19.10 and 19.11) (Gao et al., 2012). The basic idea is that a source and drain are connected to one end of a silicon or other semiconducting NW, and it is electrically isolated from surrounding media. This enables a solution, such as the cytosol of a cell, filling the nanotube to gate the transistor, enabling variation in the interior electrochemical potential to be recorded as a change in the device's conductance.

The ANTT probe was fabricated by synthesizing germanium NWs with a silicon shell by a nanocluster catalyzed VLS growth mechanism. These NWs were then

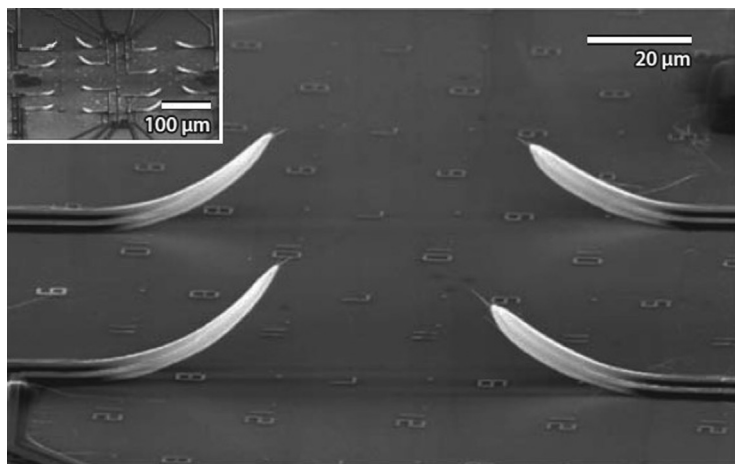


Figure 19.10 SEM image of part of an ANTT probe array fabricated from contact printed Ge/Si NWs. Inset: lower-magnification SEM image of the 4 × 4 probe array. Probe interval is about 80 μm.

Adapted from Gao et al. (2012), with permission.

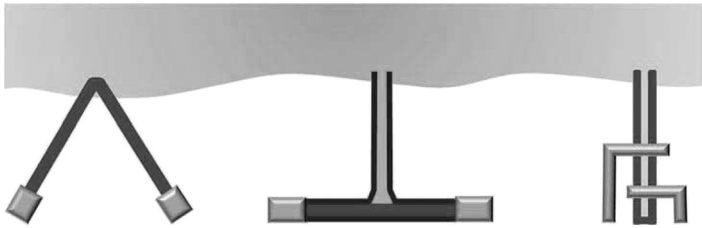


Figure 19.11 (Top) Cytosol. (Left) A kinked nanowire nanoFET. (Middle) A branched SiO₂ nanotube synthetically integrated on top of a nanoFET (BIT-FET probe). (Right) An active nanotube transistor (ANTT) probe.

Adapted from [Tian and Lieber \(2013\)](#), with permission.

contact printed onto an SU-8 layer that is on a sacrificial nickel layer. A lower SU-8 passivation layer was defined by EPL, and then metal source and drain contacts were placed, and finally the upper SU-8 passivation layer was patterned by EPL. The finished device was then freed by etching the nickel and germanium.

19.4.4.2 Device capabilities

Similar to the BIT-FET, the sensitivity of the device significantly increased after the germanium was etched ($0.1 \mu\text{S/V}$ vs $3.0 \mu\text{S/V}$), indicating that the device can record potential changes coupled through solution in the interior of the nanotube. After functionalizing the ANTT with a phospholipid bilayer, the device was placed in contact with spontaneously firing chicken cardiomyocytes. After 100 s, the recording spontaneously changed from one characteristic of extracellular cardiomyocyte action potentials to one that showed the five characteristic phases of intracellular cardiomyocyte action potentials.

Furthermore, the ANTT device showed promising results for obtaining multiplexed recordings. Probes were fabricated with two ANTT devices with a common contact source that were separated by $7.6 \mu\text{m}$ tip-to-tip. These devices simultaneously recorded the intracellular potential of a beating cardiomyocyte. It was found that the recordings were accurate, the noise from each channel was uncorrelated—indicating that there is no cross-talk between them—and that having multiple devices decreased the S/N relative to only having one device. Finally, an array of ANTT probes was created, where a forest of probes were equally spaced across a grid at well-defined distances from each other.

19.5 Future trends

NW-based devices show exciting potential to make advancements in fundamental biology research and biomedical and synthetic biology applications. NWFET probes are minimally invasive, able to make both extracellular and intracellular recordings of single cells and cell clusters, have high spatiotemporal resolution, and can be scaled

for high-density, multiplex recordings (Duan, Fu, Liu, & Lieber, 2013). There has recently been a large interest in a functional mapping of brain activities (Koch & Reid, 2012), and these properties make NW devices well suited for large-scale mapping of neural activity. One of the most remarkable properties of NW-based devices is that their material composition, and hence the corresponding device properties, can be finely and diversely tuned at the time of synthesis (Timko et al., 2010). This means the same basic methodology can be used to create devices with a large array of potential applications. To date, NW devices have made recordings from the axons and dendrites of individual neurons, heart tissue, and spontaneously beating cardiomyocytes, and the hope is that soon they will be able to directly measure the membrane potential of individual organelles (Tian & Lieber, 2013).

Two broad areas that nanoscale technologies are poised to positively affect are tissue engineering and drug delivery (Dvir, Timko, Kohane, & Langer, 2011). After the initial tissue engineering is complete, nanodevices can be used to effect desired developmental processes or record indicators of successful growth. For example, the release of angiogenic factors for new blood vessel formation could be triggered by low oxygen levels. They can also be designed to monitor the concentration of biomolecules or reactive species in real time, which is useful for reporting the condition of tissue before transplantation. Additionally, such continual monitoring can be used for triggered drug release. The idea is that the nanodevice will detect a signal (e.g., a specific antibody or high acidity), and then send a message to an embedded reserve to release a drug to treat the identified problem. Devices capable of detecting proteins at femtomolar concentrations or viruses at the single particle level have been created, and a glucose detector was successfully embedded into a rat that could one day be embedded into an insulin-secreting patch for the treatment of diabetes (Barone et al., 2009).

Finally, nanodevices could help repair tissue and organ damage. The role of biomolecule and physical cues in relation to stem cell behavior is being studied by using different biomaterials to mimic stem cell microenvironments (Lutolf, Gilbert, & Blau, 2009). Embedding nanosensors into such materials could help tease out key factors in stem cell growth, recruitment, and differentiation. It may one day even be possible to design *in vivo* nanosystems that release stem cell attractants to quickly and efficiently repair damaged tissue. Work is being done to use nanodevices to help build prosthetics to help treat spinal cord injury (Giszter, 2008) and blindness (Ahuja et al., 2011). Perhaps one day it will even be possible to bypass nervous system damage entirely by rerouting signals using a NW-based brain-machine interface (Dvir et al., 2011). Although much of this may sound like science fiction, work at the interface of NWs and biology is actually helping to make it science reality.

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